

# Phase equilibria in the Ti-rich corner of the Ti-Si-Sn-Al system

## Part I Section 9Si-1Sn (at.%)

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Phase equilibria in Ti-rich corner of the Ti-Si-Sn-Al system were studied using differential thermal analysis, X-ray diffraction, microscopy, and electron microprobe analysis. Projections of solidus and liquidus surfaces, an isothermal section at 1300°C and an isopleth at 9Si-1Sn (at.%) were constructed. It was shown that in the concentration interval studied at the solidus and 1300°C temperatures two two-phase  $Ti_5(Si,Sn,Al)_3 + (\beta-Ti)$  and  $Ti_5(Si,Sn,Al)_3 + (\alpha-Ti)$  regions are present. The liquidus surface is characterised by the regions of  $\beta$  and Z primary crystallisation, resulting in bivariant  $L \leftrightarrow \beta + Ti_5(Si,Sn,Al)_3$  eutectic. The character of horizontal and vertical sections is similar to that for the Ti-Si-Al system. © 2000 Kluwer Academic Publishers

### 1. Introduction

Titanium-rich quaternary Ti-Si-Sn-Al alloys represent significant practical interest as structural materials. The level of strength properties at elevated temperatures of the Ti-rich alloys was shown [1] to be higher than for traditional titanium alloys, particularly, for  $\alpha$ -type alloy VT-18 (81Ti-6Al-11Zr-1Mo-1Nb, mass.%). Meanwhile, some of the quaternary alloys seemed to possess elevated workability and these alloys are of practical interest in respect of combination elevated strength and ductility. Moreover, the Ti-Si-Sn-Al quaternary is one of the boundary systems for multicomponent ones, for example, for the system Ti-Si-Sn-Al-Zr-Mo, where the  $\alpha + \beta$  alloy TIMETAL 1100 (Ti-6Al-2.75Sn-4Zr-0.4Mo-0.45Si, mass.%) is of practical application. Development of new materials needs understanding of phase equilibria for the multicomponent systems. In this respect knowledge of the boundary ones is necessary.

The nature of the phase equilibria including liquid and solid phases in the Ti-rich corner of the Ti-Si-Sn-Al system was briefly mentioned in [1], but no details were given. The temperatures of phase transformations, as well as equilibria below crystallisation were not considered.

The goal of the present paper is to discuss the influence of tin on the phase equilibria in the Ti-Si-Al system. The paper considers the influence of 1 at.% Sn additions.

The edge binaries accepted in this investigation are shown in Fig. 1. The Ti-Si and Ti-Sn systems are repre-

sented according to [2], and the Ti-Al system - according to [3]. The Ti-Si and Ti-Al diagrams are modified a little as discussed in [4].

The solidus and liquidus projections and isothermal sections at 1300°C of the boundary ternaries in the Ti-corner (>50 at.% Ti) are shown in the Fig. 2. The Ti-Si-Al system (Fig. 2a, b) is given according to experimental data [4], while that for the Ti-Si-Sn (Fig. 2c, d) is according to limited experimental data [5] and evaluation of this work based on the edge binaries.

The versions of the solidus and liquidus projections and isothermal section at 1300°C for the Ti-Sn-Al system (Fig. 2e, f) are proposed based on the assessment of experimental data [6, 7]. Thus, papers [6, 7] consider the isopleths at 75 at.% Ti ( $Ti_3Al-Ti_3Sn$ ) and along the section Al : Sn = 1 : 1 (weight %), and isothermal sections at 1200, 1000, 600°C, as well. However, the proposed vertical and horizontal sections are often inconsistent with one another and with accepted version of the Ti-Al system. The original experimental results shown in [6, 7] in the most cases seem to be reliable, except the melting temperature of titanium and titanium-rich alloys (titanium melting point was measured to be 1720°C rather than accepted value 1670°C [8]), indicating of a high oxygen or nitrogen content.

The isothermal section at 900 °C of the Ti-corner of the Ti-Sn-Al system was studied in [9]. The most prominent feature is the presence of the ternary  $Ti_5Sn_2Al$  compound. The temperature and the mode of formation are unknown. These data do not correspond to

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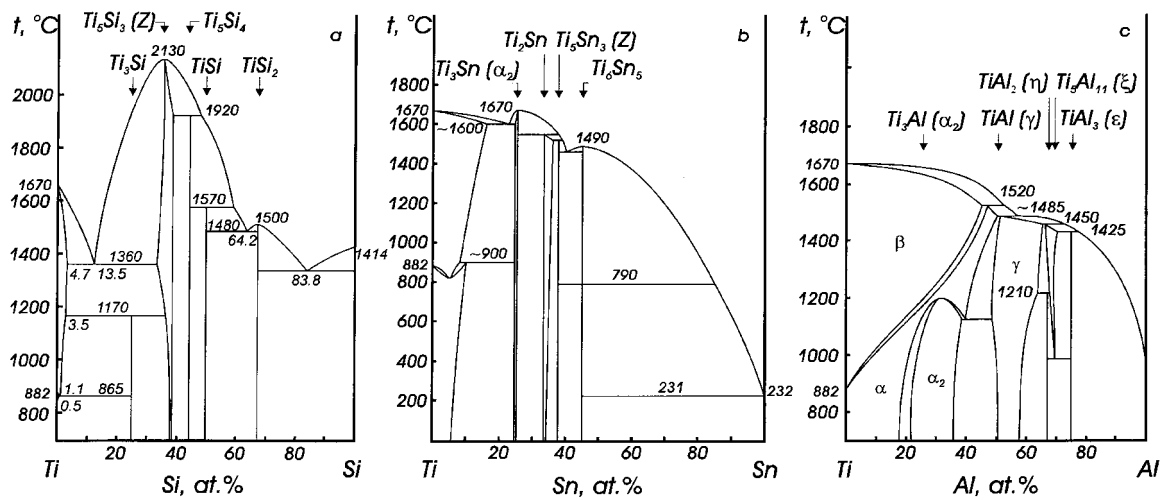


Figure 1 (a to c) Phase diagrams of the edge binary systems: (a) - Ti-Si [2], (b) - Ti-Sn [2], (c) - Ti-Al [3].

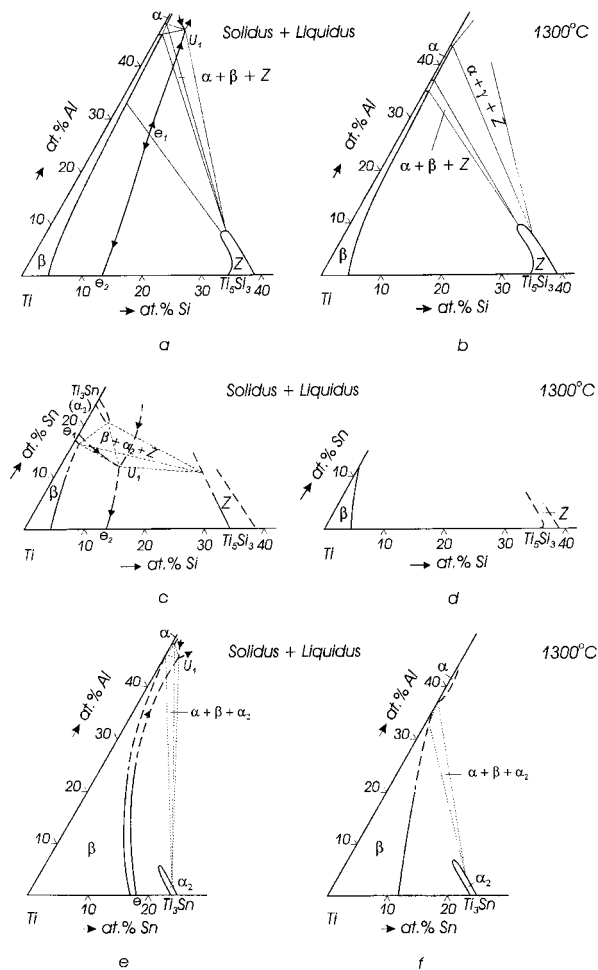


Figure 2 (a to f) Phase equilibria in the Ti-corner of the edge ternary systems: (a) - projection of liquidus and solidus surfaces of the Ti-Si-Al system [4]; (b) - isothermal section at 1300°C of the Ti-Si-Al system [4]; (c) - projection of liquidus and solidus surfaces of the Ti-Si-Sn system by [5] and evaluation of the present work; (d) - isothermal section at 1300°C of the Ti-Si-Sn system [5]; (e) - projection of liquidus and solidus surfaces of the Ti-Sn-Al system, version of this work on the basis of the assessment of data [6, 7]; (f) - isothermal section at 1300°C of the Ti-Sn-Al system, version of this work on the basis of the assessment of data [6, 7].

data [6, 7], as at the temperatures 1000 and 600°C the above ternary compound was not observed. Probably, it exists in a narrow temperature interval. In any case, this feature needs further investigation.

According to [10], the maximum solubility of Al in Ti at 700°C is 13.2 at.%, that does not correspond to the accepted Ti-Al system. Maximum joint solubility of Al and Sn in Ti was shown to be 11.1 at.% Al, 3 at.% Sn. In the assessment [11], data [6, 7] on phase equilibria in the Ti-Sn-Al system are given without any modification.

Consideration of the boundary systems shows that solidification of Ti-rich Ti-Si-Sn-Al alloys involves the liquid phase L and  $\beta$ -Ti,  $Ti_3Sn$ -,  $Ti_5(Si,Sn,Al)_3$ -based solid phases. This results in bivariate three-phase eutectic equilibria  $L \leftrightarrow \langle \beta-Ti \rangle + \langle Ti_5Si_3 \rangle$ ,  $L \leftrightarrow \langle \beta-Ti \rangle + \langle Ti_3Sn \rangle$  and  $L \leftrightarrow \langle Ti_3Sn \rangle + \langle Ti_5(Si,Sn)_3 \rangle$  and appropriate fields on the liquidus surface. These intersect giving the curve of the L-phase compositions in the monovariant four-phase  $L + \langle \beta-Ti \rangle + \langle Ti_3Sn \rangle + \langle Ti_5Si_3 \rangle$  equilibrium coming into or coming out of the invariant point of the ternary Ti-Si-Sn system. The solidus is characterised by the coexistence of  $\langle \beta-Ti \rangle$  and  $Ti_5(Si,Sn,Al)_3$ . The same solid phases should take part in equilibria at 1300°C. Below this temperature phase equilibria should be more complicated because of presence of additional  $Ti_3Al$ - and  $Ti_3Si$ -based phases.

## 2. Experimental procedure

The purity of starting rod materials was identified to be Ti - 99.85% (0.005–0.01% oxygen, 0.001–0.004% nitrogen), Al - 99.995%, Si - 99.9995%, Sn - 99.9995%. The alloys were prepared by arc-melting and subjected to X-ray, microscopy, DTA and electron microprobe (EMPA) examinations as fully discussed in [4]. The alloys were studied in the as-cast and heat treated states. The annealing was carried out in vacuum at 1300°C for 20 hours. Each specimen was placed into tantalum capsule, Zr chips were used to purify the atmosphere.

## 3. Results and discussion

For convenience the following designations are used below:  $\alpha$ ,  $\beta$  -  $\langle \alpha-Ti \rangle$  and  $\langle \beta-Ti \rangle$ -based solid solutions, respectively;  $\beta^*$  -  $\beta$ -phase transformed during cooling to  $\alpha$ ,  $\alpha_2$  or  $\gamma$ ;  $\alpha^*$  -  $\alpha$ -phase transformed during cooling to  $\alpha_2$  or  $\gamma$ ;  $\alpha_2$  -  $Ti_3Al$ - and  $Ti_3Sn$ -based phases (as these are isostructural and form continuous solid

TABLE I Phase composition of Ti-(9Si + 1Sn)-Al alloys according to the results of this investigation

Alloys composition, at.%			Phase constitution of the alloys	
Ti	Al	Heat treatment	Deduced from overall experimental and literature data	Observed at room temperature by X-ray method
90	0	As-cast	$\beta^{*1)} + \text{eutectic } (\beta^* + Z)$	-
		Annealed 1300°C, 20h	$\beta + Z$	$\alpha + Z$
85	5	As-cast	$\beta^* + \text{eutectic } (\beta^* + Z)$	$\alpha + Z$
		Annealed 1300°C, 20h	$\beta + Z$	$\alpha + Z$
80	10	As-cast	$\beta^* + \text{eutectic } (\beta^* + Z)$	$\alpha + Z$
		Annealed 1300°C, 20h	$\beta + Z$	$\alpha + Z$
75	15	As-cast	$\beta^* + \text{eutectic } (\beta^* + Z)$	$\alpha/\alpha_2 + Z$
		Annealed 1300°C, 20h	$\beta + Z$	$\alpha/\alpha_2 + Z$
70	20	As-cast	Eutectic ( $\beta^* + Z$ )	$\alpha/\alpha_2 + Z$
		Annealed 1300°C, 20h	$\beta + Z$	$\alpha_2 + Z$
65	25	As-cast	$Z + \text{eutectic } (\beta^* + Z)$	$\alpha/\alpha_2 + Z$
		Annealed 1300°C, 20h	$\beta + Z$	$\alpha_2 + Z$
60	30	As-cast	$Z + \text{eutectic } (\beta^* + Z)$	$\alpha_2 + Z$
		Annealed 1300°C, 20h	$\alpha + Z$	$\alpha_2 + \gamma + Z$
54	36	As-cast	$Z + \text{eutectic } (\beta^* + Z)$	$\gamma + Z$
		Annealed 1300°C, 20h	$\alpha + \gamma + Z$	$\alpha_2 + \gamma + Z$

<sup>1)</sup> $\beta^*$  -  $\beta$ -phase transformed during cooling to  $\alpha$ ,  $\alpha_2$  or  $\gamma$ .

<sup>2)</sup>As  $\alpha$ - and  $\alpha_2$ -phases can be poorly distinguished by X-ray method, presence of either or both phases is possible.

TABLE II Temperatures of phase transformations measured in as-cast Ti-(9Si + 1Sn)-Al alloys

Alloys composition, at.%			Temperatures °C, according to DTA			
Ti	Al	Specimen weight, g	Liquidus	Solidus	Solid state transformation	
					$\alpha \leftrightarrow \beta$	$\alpha \leftrightarrow \alpha_2$
85	5	0,08	1530 ↓ <sup>1)</sup>	1395	940	-
80	10	0,09	1510 ↓	1455	1030	-
75	15	0,14	1515 ↓	1480	1100	770
70	20	0,12	-	1515	1200	-
65	25	0,05	1600 ↓	1515	-	1205
60	30	0,08	-	1480	1330	-
54	36	0,05	-	1415	-	-

<sup>1)</sup>Temperatures marked ↓ correspond to DTA data at cooling, other data correspond to DTA data at heating.

solution at the temperatures lower than the solidus they are named here identically);  $\gamma$  - TiAl-based phase;  $Z$  -  $\text{Ti}_5(\text{Si}, \text{Sn}, \text{Al})_3$ - based phase (as  $\text{Ti}_5\text{Si}_3$  and  $\text{Ti}_5\text{Sn}_3$  are isostructural, one can expect a continuous solid solution in the whole temperature interval).

Compositions of the quaternary Ti-Si-Sn-Al alloys studied in this investigation are based on the ternary Ti-Si-Al alloys containing 10 at.% Si [4], where 1 at.% Si is substituted for Sn. Thus, the alloys studied contained 9Si-1Sn (at.%), aluminium content changed from 0 to 36 at.% in intervals of 5 at.%.

The results obtained are shown in Tables I, II and in the Figs 3–5. The phase constitution of the alloys is shown in the Table II. As can be seen, the actual phase constitution on solidification and at 1300°C often differs from that observed by the X-ray method at room temperature. This is due to the fact that  $\beta \rightarrow \alpha$ ,  $\beta \rightarrow \alpha \rightarrow \alpha_2$ ,  $\alpha \rightarrow \alpha_2$ ,  $\alpha \rightarrow \alpha_2 + \gamma$  solid-state transformations are so fast that high temperature phases cannot be kept at cooling the samples. Also, the boundaries of the homogeneity regions of the phases taking part in phase equilibria are very temperature dependent. Thus, after cooling the specimens within the furnace (~5–10°C/sec) their compositions appear in the phase regions, which do not correspond to the high temperature state. So, the actual phase constitution at the high tem-

peratures (Table I) was stated on the basis of the totality of the experimental results taking into account the character of the boundary systems (Figs 1, 2).

The liquidus and solidus projections and isothermal section at 1300°C resulted from this investigation are shown in Fig. 3. They are given as projections of appropriate surfaces on the triangle Ti-Al-(Si + Sn). One of the axes reflects the joint concentration of silicon and tin. Here silicon and tin together are considered as one component, and the system is considered as ternary. In this case tie-lines lie in or virtually in the triangle plane. This way of presentation seems to be acceptable for that part of the system, where the character of phase equilibria is similar to that in the Ti-Si-Al system.

Projection of the solidus and liquidus surfaces is shown in the Fig. 3a. The equilibria at solidus temperatures are characterised by wide two-phase  $\beta + Z$  region similar to the ternary Ti-Si-Al system. In the  $\beta + Z$  region the solidus surface has a temperature maximum at 1515°C, corresponding to the invariant pseudobinary eutectic  $L \leftrightarrow \beta + Z$  with the eutectic point  $e_1$  at ~68Ti-9(Si + Sn)-23Al, at.% (1545°C, 65Ti-8Si-27Al, at.%, for the ternary Ti-Si-Al system [4]). The temperatures of phase transformations are shown in Table II.

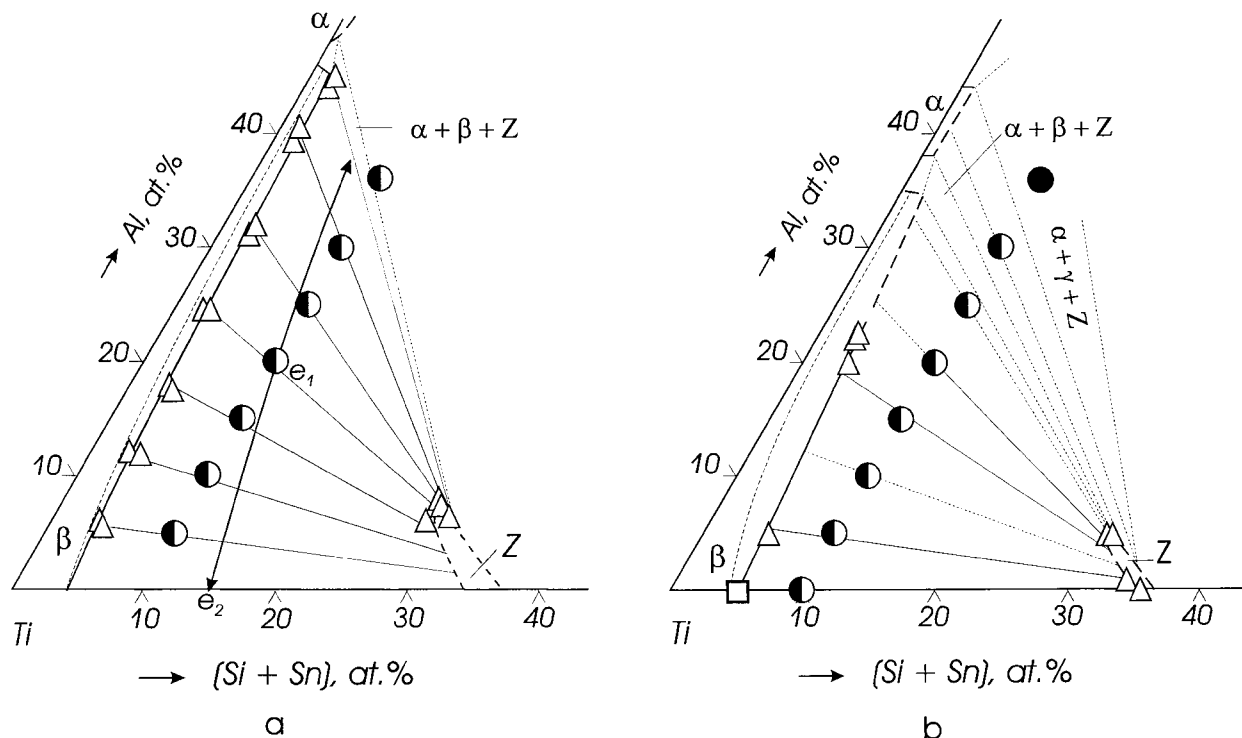


Figure 3 (a and b) Phase equilibria in the Ti-corner of the Ti-Si-Sn-Al system resulting from this investigation: (a) projection of liquidus and solidus surfaces; (b) isothermal section at 1300°C:  $\square$  - data from the literature;  $\Delta$  - EMPA results;  $\bullet$  - two-phase sample;  $\bullet$  - three-phase sample; - - -  $\beta$ -phase boundary for the ternary Ti-Si-Al system.

The liquidus surface is characterised by the fields of  $\beta$  and Z primary crystallisation resulting in three-phase eutectic  $L \leftrightarrow \beta + Z$  equilibrium. In the quaternary system three-phase equilibria are bivariant, and compositions of the liquid phase taking part in the equilibria represent the surface. However, in the type of presentation used here, the above equilibrium degenerates to monovariant, and liquid phase compositions give the curve.

The location of the  $L \leftrightarrow \beta + Z$  eutectic curve was determined by the microstructural examination of as-cast alloys (see Fig. 4). The alloys with less than 20 at.% Al are hypo-eutectic, with  $\beta$  primary crystallisation (Fig. 4a, b), the alloys containing more than 20 at.% Al are hyper-eutectic with Z primary crystallisation (Fig. 4d, e). This is similar to the ternary Ti-Si-Al alloys [4]. The alloy 70Ti-(9Si + 1Sn)-20Al is of eutectic nature (Fig. 4c), while the alloy 70Ti-10Si-20Al is hyper-eutectic. So, considering now the quaternary system by a tetrahedron, the surface of the L-phase compositions for bivariant  $L \leftrightarrow \beta + Z$  eutectic originates from the appropriate monovariant curves of the ternary systems Ti-Si-Al and Ti-Si-Sn. Titanium content in the quaternary eutectic L is less than in the Ti-Si-Al ternary L, when Al content is the same.

A complicated microstructure is observed for the alloy containing 36 at.% Al (Fig. 4e). The lamellar-type matrix results from the solid-state transformation of  $\beta$  (or  $\alpha$ ) to  $\gamma$ , as observed for the Ti-Si-Al [4] and Ti-Si-Ge-Al [12] systems. At the solidus temperature this alloy is more probably located in two-phase  $\alpha + Z$  region, similar to the Ti-Si-Al ternary. However, it may be located in the three-phase  $\beta + \alpha + Z$  region.

The isothermal section at 1300°C (Fig. 3b) is similar to the solidus surface (Fig. 3a) and is characterised by coexistence of Z-phase with  $\alpha$  and  $\beta$ . The typical microstructures of heat treated at 1300°C alloys are shown in the Fig. 4f, g. Microstructure of the annealed at 1300°C alloy 70Ti-(9Si + 1Sn)-20Al (Fig. 4f) contains two phases:  $\beta^*$  and Z, in contrast to the eutectic microstructure of the as-cast alloy (Fig. 4c). To compare the microstructures of as-cast and annealed at 1300°C 54Ti-(9Si + 1Sn)-36Al alloy (Fig. 4e and g, respectively), no eutectic is observed for the annealed sample. Three phases, Z (large grains),  $\alpha^*$  (uncracked part of the matrix) and  $\gamma$  (cracked part of the matrix), are observed.

The isopleth at 9Si-1Sn (at.%) is shown in the Fig. 5. Its character is similar to those for the ternary Ti-Si-Al system at 10 at.% Si [4]. The shape of the  $\alpha_2 + Z$  field is shown to be similar to that in the ternary Ti-Si-Al system. The region of  $\alpha_2$ -phase existence is supported by the presence of  $\alpha_2$ -phase reflections in X-ray patterns of the annealed alloys having more than 15 at.% Al (see Table I). The character of the  $\alpha \leftrightarrow \beta$  transformations in the region 0–5 at.% Al can be more complicated than in the Fig. 5. The version given here is based on the isopleth at 90 at.% Ti of the Ti-Si-Sn system [5].

The measured values of solubility for the as-cast alloys were taken as representing the values at the solidus, as discussed in [4]. At the solidus temperature, the  $\beta$ -homogeneity region stretches from  $\sim 4.5$  at.% Si, 1.5 at.% Sn and 0 at.% Al to  $\sim 2$  at.% (Si + Sn) and  $\sim 45$  at.% Al. At 1300°C it stretches from  $\sim 5$  at.% (Si + Sn), 0 at.% Al to  $\sim 2$  at.% (Si + Sn),  $\sim 34$  at.% Al. As discussed in [1], the silicon solubility

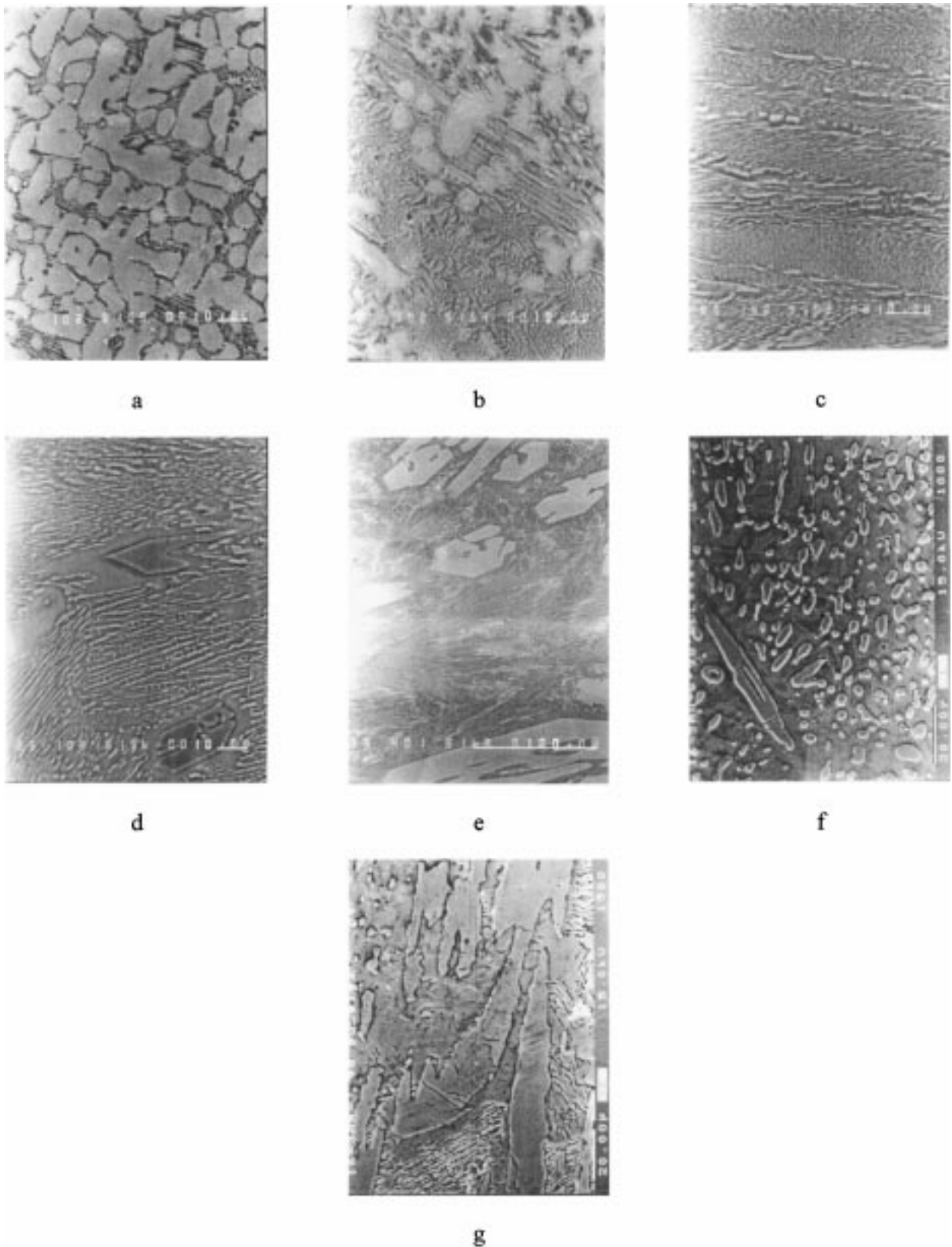


Figure 4 (a to g) Microstructures of Ti-(9Si+1Sn)-Al samples: (a) 85Ti-(9Si+1Sn)-5Al, as-cast,  $\times 1000$ ;  $\beta^*$  + eutectic ( $\beta^* + Z$ ); (b) 75Ti-(9Si+1Sn)-15Al, as-cast,  $\times 1000$ ;  $\beta^*$  + eutectic ( $\beta^* + Z$ ); (c) 70Ti-(9Si+1Sn)-20Al, as-cast,  $\times 1500$ ; Eutectic ( $\beta^* + Z$ ); (d) 65Ti-(9Si+1Sn)-25Al, as-cast,  $\times 1000$ ; Z + eutectic ( $\beta^* + Z$ ); (e) 54Ti-(9Si+1Sn)-36Al, as-cast,  $\times 400$ ; Z + eutectic ( $\beta^* + Z$ ); (f) 70Ti-(9Si+1Sn)-20Al, annealed  $1300^\circ\text{C}$ ,  $\times 1000$ ;  $\beta^* + Z$ ; (g) 54Ti-(9Si+1Sn)-36Al, annealed  $1300^\circ\text{C}$ ,  $\times 1500$ ;  $\alpha^* + \gamma + Z$ .  $\alpha^*$  -  $\alpha$  phase transformed during cooling to  $\alpha_2$  or  $\gamma$ .

in the  $\beta$ -phase at solidus temperatures is lower than that of tin. The homogeneity range of the ternary Ti(Si,Al)  $\beta$ -phase is narrower than that for the quaternary Ti(Si,Sn,Al)  $\beta$ -phase. The same is observed in this investigation at  $1300^\circ\text{C}$ . The homogeneity range of the ternary Ti(Si,Al)  $\beta$ -phase is shown in the Fig. 3

by the dotted lines. Solubility of Si and Sn in  $\alpha$ - and  $\gamma$ -phases was not determined in this work and should be studied additionally.

The solidus projection and isothermal section at  $1300^\circ\text{C}$  (Fig. 3a and b, respectively) show the maximum aluminium solubility in Z-phase to be about

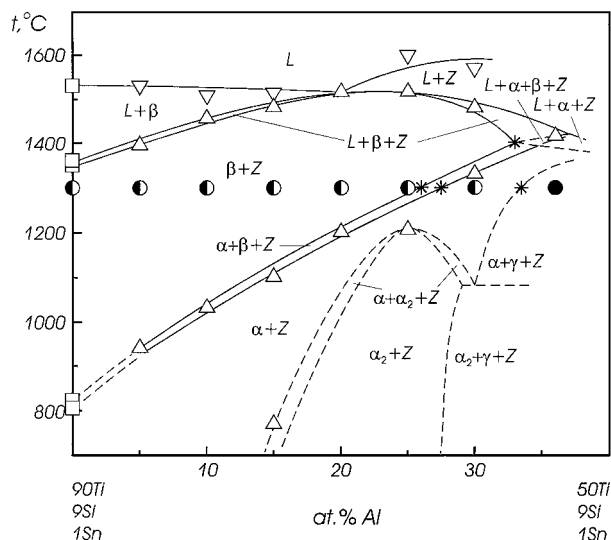


Figure 5 Isopleth at 90 at.% Ti of titanium corner of Ti-Si-Sn-Al system: ● - two-phase sample, ● - three-phase sample, Δ, ∇ - DTA data at heating and cooling, respectively, □ - data [5]; \* - the boundaries of the phase fields taken from the horizontal sections.

7.5 at.% and 5 at.% (about 9 at.% for the ternary  $Ti_5(Si,Al)_3$  compound), correspondingly. Tin solubility for both cases is less than 0.5 at.%.

#### 4. Conclusions

- Phase equilibria between solidus and liquidus and at 1300°C are studied by the methods of DTA, X-ray, metallography and EMPA analyses. The solidus-liquidus projection, isothermal section at 1300°C and isopleth at 9Si-1Sn were constructed.

- Substitution of 1 at.% Si for Sn does not change the character of phase equilibria in the concentration interval studied.
- The difference between the Ti-Si-Sn-Al and Ti-Si-Al systems involves both the extents of the homogeneity regions of individual phases, and the temperatures of phase transformations.

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