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Abstract

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INVESTIGATION OF PHASE EQUILIBRIUM IN THE QUASI-TERNARY SYSTEM Ti–Ti_3Sn–Zr

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As is known, zirconium is an electronic analogue of titanium. Between the α- and β-modifications of zirconium and titanium, respectively, there exists unlimited mutual solubility.

M. K. McQuillan ([1]), and also we ourselves ([2]), established the existence of a continuous series of solid solutions between the α-modification of titanium and the compound Ti_3Sn (γ-phase) in the binary titanium-tin system.

The existence of a continuous series of solid solutions between the α-modification of zirconium and the compound Ti_3Sn was also established by us in studying phase equilibrium in the quasi-binary system Ti_3Sn–Zr ([3]).

Thus, in the ternary titanium–zirconium–tin system, the binary system Ti_3Sn–Zr delimits a region of compositions adjacent to the titanium corner, in which, at low temperatures, judging from the character of phase equilibrium in the above-mentioned binary systems, there should exist a continuous series of solid solutions based on the α-modification of titanium (zirconium, γ-phase).

The present work is devoted to the study of phase equilibrium in this region of compositions, which may be regarded as the quasi-ternary system Ti–Ti_3Sn–Zr.

To carry out the assigned task, a total of 74 alloys of different composition were prepared (see Table 1).

As starting materials for preparing the alloys, magnesiothermic titanium (99.89% Ti), iodide zirconium (99.9% Zr), and tin of 99.9% Sn purity were used.

All alloys were prepared by the method of crucibleless induction melting in suspension in an atmosphere of purified helium ([4]). This method of preparing alloys based on titanium and zirconium, as was found by us in a special investigation, has definite advantages over other methods, since it ensures the production of alloys purer with respect to the content of gases and other impurities, and also more homogeneous in composition, which makes it possible to

shorten substantially the time of heat treatment of the alloys in order to bring them to equilibrium in the investigation of phase diagrams ([5]).

Cast alloy specimens were subjected to deformation by 10-20%, with the exception of alloys close in composition to the γ-phase, and were annealed at 850 and 800° for a total of 2700 hours. Annealing was carried out in quartz ampoules with double walls, evacuated to 10^{-4} mm Hg. Between the walls, pure titanium sponge was placed as a getter. This annealing technique completely eliminated the possibility of contamination of the alloys due to diffusion of air through quartz at high temperatures.

To study phase equilibrium in the system under consideration, Ti–Ti_3Sn–Zr, the method of microscopic analysis was applied to specimens quenched from various temperatures.

Table 1

Chemical composition of the alloys studied (in weight percent)

Alloy No.	Sn	Zr	Ti	Alloy No.	Sn	Zr	Ti	Alloy No.	Sn	Zr	Ti
1	–	–	100	26	43	5	bal.	51	5	95	bal.
2	5	–	bal.	27	38	15	»	52	15	5	»
3	10	–	»	28	36	20	»	53	15	10	»
4	15	–	»	29	34	25	»	54	15	15	»
5	20	–	»	30	27	40	»	55	15	25	»
6	25	–	»	31	25	45	»	56	15	40*	»
7	30	–	»	32	22.5	50*	»	57	15	61*	»
8	35	–	»	33	16	65*	»	58	15	65*	»
9	40	–	»	34	11.5	75*	»	59	15	70*	»
10	41.8*	–	»	35	9	80*	»	60	25	5*	»
11	44.8*	–	»	36	7	85*	»	61	25	15*	»
12	50.0*	–	»	37	5	89*	»	62	25	20	»
13	–	5	»	38	5	5	»	63	25	25	»
14	–	10	»	39	5	10	»	64	25	30	»
15	–	15	»	40	5	15	»	65	25	35	»
16	–	20	»	41	5	20	»	66	25	50	»
17	–	25	»	42	5	25	»	67	35	5	»
18	–	30	»	43	5	30	»	68	35	10	»
19	–	40	»	44	5	40	»	69	35	15	»
20	–	50	»	45	5	50	»	70	40	5	–
21	–	60	»	46	5	60*	»	71	20	80	–
22	–	70	»	47	5	70*	»	72	15	85	–
23	–	80	»	48	5	75*	»	73	10	90	–
24	–	90	»	49	5	80*	»	74	–	100	
25	–	95	»	50	5	90*	»				

Fig. 1. Isothermal section at 500°. 1 –$\alpha(\gamma)$

Figure 1: Fig. 1. Isothermal section at 500°. 1 –$\alpha(\gamma)$

Fig. 2. Isothermal section at 800°. 1 –$\alpha(\gamma)$; 2 –β; 3 –$\alpha(\gamma) + \beta$

Figure 2: Fig. 2. Isothermal section at 800°. 1 –$\alpha(\gamma)$; 2 –β; 3 –$\alpha(\gamma) + \beta$

Note. A selective chemical analysis carried out on alloys marked with an asterisk (20 alloys) showed insignificant deviations (in tenths of a percent) from the calculated composition. Therefore the table gives the calculated composition.

After homogenization at 800°, all alloys were annealed for 1000 h at a temperature of 500°, which is below the allotropic-transformation temperature of titanium and zirconium, and also below the minimum temperature in the titanium–zirconium system. After annealing the alloys were quenched in water.

Fig. 1. Isothermal section at 500°.
1 –$\alpha(\gamma)$

Fig. 2. Isothermal section at 800°.
1 –$\alpha(\gamma)$; 2 –β; 3 –$\alpha(\gamma) + \beta$

Microscopic analysis of the quenched specimens showed that all of them are single-phase and have a polyhedral $\alpha(\gamma)$ structure.

It follows from Fig. 1, which presents the isothermal section at 500°, that throughout the investigated concentration range of the quasi-ternary system Ti –Ti_3Sn–Zr there exists a continuous series of solid solutions.

Figure 2 presents the isothermal section at 800°, i.e., at a temperature below the allotropic transformation temperature of titanium and zirconium, but above the temperature of the minimum in the titanium–zirconium system. As was to be expected, at this temperature a two-phase region $\alpha(\gamma) + \beta$ appears, separating the two single-phase $\alpha(\gamma)$ and β regions. The microstructure of alloys

Fig. 3. Isothermal section at 1000°. The designations are the same as in Fig. 2

Fig. 4. Isothermal section at 1560°.
1 –L; 2 –L + $\alpha(\gamma)$; 3 –L + β; the remaining designations are the same as in Figs. 1-3

quenched from 800° and corresponding in composition to the $\alpha(\gamma) + \beta$ region is a mixture of $\alpha(\gamma)$ and α' crystals. Alloys quenched from this temperature and corresponding in composition to the β region have an α' structure.

Fig. 3 and Fig. 4

Figure 3: Fig. 3 and Fig. 4

After annealing at temperatures of 800 and 500° and carrying out the corresponding investigations, all alloys were annealed at 1000, 1200, and 1560°, respectively, for 1700, 100, and 2 h.

Figure 3 presents the isothermal section at 1000°, i.e., at a temperature exceeding the allotropic transformation temperature of both titanium and zirconium. As follows from this figure, the β region expands in comparison with the preceding section, while the $\alpha(\gamma)$ region narrows noticeably. The microstructure of alloys quenched from 1000° and lying, by composition, in the corresponding phase regions is analogous to that described for the preceding section.

The isothermal section at 1200° differs practically in no way from the section at 1000°; therefore we do not present it here.

Figure 4 presents the isothermal section at a temperature of 1560°*, which is below the eutectic-transformation temperature in the titanium–tin system (1590°), but above the eutectic-transformation temperature in the Ti_3Sn–Zr system (1540°). It follows from this figure that, in addition to the regions $\alpha(\gamma)$, $\alpha(\gamma)+\beta$, and β (the structure of alloys quenched from these regions is analogous to that described for the preceding sections), new phase regions appear: L, $L + \alpha(\gamma)$, $L + \beta$, and $L + \alpha(\gamma) + \beta$. The liquid phase L in the structure of quenched alloys corresponding in composition to the two-phase regions $L+\alpha(\gamma)$ and $L + \beta$, as well as to the three-phase region $L + \alpha(\gamma) + \beta$, appears as typical melting. The remaining structural constituents in these alloys appear

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* Heat treatment of the alloys at 1560° was carried out by heating the alloys placed in zirconia crucibles.

as described above. The alloy containing 25 wt.% titanium, 25 wt.% tin, and 50 wt.% zirconium melted completely.

From consideration and comparison of the isothermal sections presented in Figs. 1-4, it may be concluded that at low temperatures (below the temperature of the minimum in the titanium–zirconium system) the phase equilibrium in the quasi-ternary system Ti–Ti_3Sn–Zr is described by a phase diagram with a continuous series of solid solutions.

At higher temperatures the phase equilibrium is described by a spatial complex characterizing a ternary phase diagram composed of three binary diagrams, of which (β-Ti)–Ti_3Sn and Ti_3Sn–(β-Zr) are eutectic-type diagrams with limited solubility in the solid state, while one, (β-Ti)–(β-Zr), is a phase diagram with a continuous series of solid solutions. Such a diagram is a typical one [6]; therefore, having an idea of the character of the phase equilibrium at the five above-mentioned temperatures, it is not difficult to establish it for all other temperatures by means of simple geometric constructions.

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Note: Figure translations are in progress. See original paper for figures.