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INVESTIGATION OF PHASE EQUILIBRIUM IN THE SYSTEM Ti_3Sn–Zr

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In works ([1], [2]) it was shown that in the binary titanium–tin system, between the low-temperature modification of titanium and the chemical compound Ti_3Sn, a continuous series of solid solutions is formed. At the same time, a very favorable relationship was noted between the atomic radii in the lattices of α-Ti and Ti_3Sn (for coordination number 12). It is known that zirconium is the closest analog of titanium; both between the α- and between the β-modifications of zirconium and titanium there exists unlimited mutual solubility ([3]). A comparative analysis of the structures of α-Zr and Ti_3Sn shows that they also satisfy the basic requirements ([4]) for the formation of a continuous series of solid solutions.

In this connection, the study of phase equilibrium in alloys whose representative points lie on the Ti_3Sn–Zr section of the concentration triangle Ti–Zr–Sn is of definite theoretical interest.

From the practical point of view, this investigation is useful in connection with the possibility of finding new alloy compositions possessing interesting physicochemical properties. To carry out the task set in the work, alloys of zirconium with the compound Ti_3Sn were prepared. The composition of the alloys according to chemical-analysis data is given in Table 1.

Table 1

Chemical composition of the alloys investigated (wt. %)

Alloy Nos.	Ti	Zr	Sn	Alloy Nos.	Ti	Zr	Sn
1	51.9	4.9	43.2	9	27.6	49.9	22.5
2	49.2	10.0	40.8	10	24.4	55.0	20.6
3	47.2	14.7	38.1	11	19.6	64.3	16.1
4	44.2	19.9	35.9	12	14.6	74.0	11.4
5	40.8	25.0	34.2	13	11.9	79.2	8.9
6	37.4	30.1	32.5	14	8.4	84.6	7.0
7	32.9	39.9	27.2	15	5.5	89.4	5.1
8	30.3	44.8	24.9	16	3.4	94.1	2.5

As starting materials for preparing the alloys, magnesiothermic titanium of grade TG-00 (99.8% Ti), iodide zirconium (99.9% Zr), and a Ti–Sn master alloy containing 67.5% tin were used. The alloys were prepared by the method of induction crucibleless melting in the suspended state (^{5}). This is the most favorable method for obtaining alloys in investigations of phase diagrams, allowing the time of homogenizing annealing needed to bring them to an equilibrium state to be considerably shortened (^{6}).

The cast alloys were subjected to deformation (approximately 20%) (with the exception of alloys close in composition to the compound Ti_3Sn) and to homogenizing annealing at 800°. The specimens were placed in ampoules evacuated to 10^{-4} mm Hg.

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Fig. 1. Microstructures of some alloys of the Ti_3Sn–Zr system after annealing and quenching in water.
a –30 wt.% Zr at 800° (polyhedral structure $\gamma(\alpha)$);
b –30 wt.% Zr at 1000° (two-phase structure $\gamma+\beta$);
c –50 wt.% Zr at 1000° (two-phase structure $\gamma+\beta$);
d –80 wt.% Zr at 1000° (single-phase acicular structure α').
200×

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Fig. 2. *a* –leptochlorite-oolitic marl; sideritization (*c*) of oolites and weak pyritization (*n*) of the cement are observed (specimen No. 1188).
b –hydrogetite-oolitic sideritized (*c*) marl; contains a partially oxidized, semitransparent fragment of oolitic rock (×) (specimen No. 1190a).
c –leptochlorite oolites in sideritized (*c*) clayey-silty cement of gravelite; the siderite is considerably oxidized, semitransparent (specimen No. 1191).
Parallel nicols, 67×

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Fig. 4. Debyegrams of celadonite (*a*) and perovskite (*b*)

and sealed quartz ampoules. In order to prevent diffusion of air through the quartz, the ampoules containing the specimens were sealed into evacuated ampoules of larger diameter; in the spaces between the ampoules, a clean titanium sponge was placed as a getter. This procedure completely eliminated the possibility of contamination of the alloys by gases during annealing. The homogenized alloys were examined under a microscope. As an etchant for revealing the microstructure, a mixture consisting of one part HNO_3, one part HF, and two parts glycerin (by volume) was used.

Microscopic analysis of the alloys after annealing for 1500 h at 800° showed that they are all single-phase and have a polyhedral structure.

Fig. 2. Dependence of hardness on the composition of Ti_3Sn–Zr alloys after annealing at 800, 1000, and 1200° and quenching in water (curves 1, 2, 3,

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Fig. 3. Quasibinary phase diagram of Ti_3Sn—Zr

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respectively).

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This indicates the existence of a continuous series of solid solutions between α-zirconium and the compound Ti_3Sn. After annealing at 800°, all alloys were successively annealed at 1000° and 1200° for 150 and 200 h, respectively, and quenched from the indicated temperatures in water. Microscopic analysis of the quenched specimens gave the following picture of phase equilibrium in the system under study at the indicated temperatures. Up to ~22 wt.% zirconium, all alloys are single-phase and have a polyhedral structure, practically no different from that which was observed after annealing at 800°. Beginning with this concentration, a further increase in the zirconium content leads to the appearance of a second phase in the alloy structure, the amount of which increases regularly. Beginning at approximately 55% zirconium, the second phase has the α' structure. Alloys quenched from 1000° and 1200° and containing 80 wt.% zirconium and more have a single-phase α' structure. Figure 1 shows microstructures of several alloys illustrating the described picture of phase equilibrium in the Ti_3Sn —Zr system.

Figure 2 presents the dependence of hardness on the composition of Ti_3Sn—Zr alloys quenched after annealing at 800, 1000, and 1200°. Hardness measurements were performed on a Vickers instrument under a load of 10 kg. It follows from Fig. 2 that the dependence of hardness on the composition of alloys quenched from 800° (curve 1) is characterized by a smooth curve with a maximum and is typical of systems with a continuous series of solid solutions, whereas the analogous dependences for alloys quenched from 1000 and 1200° (curves 2 and 3), characterize a miscibility gap; moreover, in the two-phase region the hardness changes practically according to the law of additivity. Breaks in the curves of hardness as a function of the composition of alloys quenched from 1000 and 1200° make it possible to outline the boundary separating the regions γ and $\gamma + \beta$, as well as $\gamma + \beta$ and β.

On the basis of microscopic-analysis data, as well as hardness measurements, it may be concluded that the Ti_3Sn—Zr section of the ternary Ti—Zr—Sn system is quasibinary.

To construct the quasibinary phase diagram of Ti_3Sn—Zr, the method of high-temperature noncontact thermal analysis was used; it is distinguished by high sensitivity and makes it possible to determine the temperatures of phase transitions up to 3000° (7-9).

Alloy specimens weighing 1-2 g were placed in crucibles made of zirconium oxide. Heating was carried out in an atmosphere of purified helium, with which the furnace chamber was filled after evacuation to $\sim 10^{-5}$ mm Hg. The thermograms were recorded in coordinates of the temperature difference between specimen and standard—time. On the thermograms taken for the Ti_3Sn—Zr alloys, as a rule, two thermal effects were observed. In alloys containing 30.1% and 39.9 wt. % Zr, three thermal effects were observed, and in the alloy with 49.9% Zr only one thermal effect at 1540°.

Table 2

Temperatures of phase transformations in Ti_3Sn—Zr alloys (in °C)

Alloy composition, wt. %	I	II	III
10	1660	1620	–
19.9	1648	1565	–
30.1	1627	1540	1000
39.9	1600	1545	895
49.9	–	1540	–
55.0	1620	1543	–
64.3	1700	1540	–
74.0	1780	1542	–
94.1	1835	1731	–

Table 2 gives the temperatures of the thermal effects observed on the thermograms in the study of the Ti_3Sn—Zr alloys.

The equilibrium quasibinary diagram Ti_3Sn—Zr, constructed from these data and also from data of investigations of the microstructure and hardness of the alloys, is shown in Fig. 3.

It should be noted that up to the present time the liquidus lines in phase diagrams based on titanium and zirconium have practically not been constructed, owing to the difficulties in carrying out thermal analysis of such high-temperature and chemically active materials. Therefore, in the reference literature on the diagrams of titanium and zirconium the liquidus lines, as a rule, are given as dashed lines.

The use of noncontact thermography in the present case made it possible, in addition to determining the solidus points and phase transitions in the solid

Fig. 4. Triangulation of the ternary system titanium—zirconium—tin

Figure 3: Fig. 4. Triangulation of the ternary system titanium—zirconium—tin

state, also to record the liquidus temperatures corresponding to the precipitation of primary γ and β crystals.

It follows from Fig. 3 that the equilibrium between the β modification of zirconium and the compound Ti_3Sn is described by a phase diagram of the eutectic type with limited solubility in the solid state. The temperature of the eutectic transformation is $\sim 1540°$; the concentration of the eutectic point corresponds to ~ 50 wt. % Zr. Between the α modification of zirconium and the compound Ti_3Sn a continuous series of solid solutions is formed.

If the diagram obtained is compared with the Ti_3Sn—Ti diagram, the similarity of the geometric images describing the phase equilibrium in these systems is striking; this indicates, to a known extent, a far-reaching chemical analogy between titanium and zirconium. It should be noted, however, that in order to attain equilibrium and to obtain all alloys as single-phase at 800° in the Ti_3Sn —Ti system, a very prolonged homogenizing anneal is required, whereas in the Ti_3Sn—Zr system equilibrium is reached much more readily. This apparently indicates that the diffusion rate in the Ti_3Sn—Zr system at the corresponding temperatures is significantly higher.

On the basis of the fact that the investigated section Ti_3Sn—Zr of the ternary phase diagram Ti—Zr—Sn is quasibinary, it is possible to triangulate this system ([10,11]) (see Fig. 4). The figurative point corresponding to the compound Ti_3Sn is a node in this part of the diagram. Consequently, in addition to the Ti_3Sn—Zr section, the sections Ti_3Sn—Zr_4Sn and Ti_3Sn—Zr_5Sn_3 must probably actually exist. The part of the Ti—Zr—Sn phase diagram enclosed in the triangle Ti—Ti_3Sn—Zr, at low temperatures, consists of continuous solid solutions. At higher temperatures, evidently, there will be a miscibility gap and the equilibrium will become two-phase: $\gamma + \beta$; moreover, the structure, depending on the alloy concentration, must be either $\gamma +$ eutectic $(\gamma + \beta)$ or $\beta +$ eutectic $(\gamma + \beta)$*.

Fig. 4. Triangulation of the ternary system titanium—zirconium—tin

Thus, by methods of microscopic and thermal analysis, as well as by hardness measurements of the alloys, the phase equilibrium in the Ti_3Sn—Zr system has been investigated; it has been shown that the Ti_3Sn—Zr system is quasibinary; on the basis of general theoretical considerations the existence of a continuous series of solid solutions between the low-temperature modification of zirconium and the compound Ti_3Sn has been proved. The triangulation of the ternary titanium—zirconium—tin system has been carried out, as a result of which further development of this system will be considerably facilitated.

In conclusion, we express our gratitude to the author of the contactless thermography method, N. A. Nedumov, for assistance in carrying out the thermal analysis of the alloys of this system.

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* The structure after crystallization is meant, since after heating single-phase alloys at low temperatures the eutectic structural constituent is absent, and only the corresponding second phase appears.

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

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