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Letter to the Editors

The Sn–Ti–Zr system: equilibrium phases at 900°C

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Abstract

Sn–Ti–Zr alloys were obtained by melting pure elements in an arc furnace. The compositions of the alloys were selected in order to establish the equilibria and domains of the stable phases. Isothermal heat treatments at 900°C were made in two time intervals of 750 h, each one performed in order to reach the stable equilibria of the phases. The characterization of the phases and the determination of their compositions were made by metallographic observations, X-ray diffraction, energy dispersive spectroscopy and electron microprobe analysis. The isothermal section of the Sn–Ti–Zr system at 900°C was drawn in a Gibbs phase diagram.

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1. Introduction

The knowledge of the properties of the Sn–Zr system is relevant in the nuclear-power technology because tin is a key element in the design of Zr-base alloys, since it increases their strength and corrosion resistance. Many critical components for the nuclear power reactors are manufactured employing this kind of materials.

Titanium and zirconium, being elements with high affinity, form solid solutions in the complete range of compositions of both structures, hexagonal closed-packed and body-centered cubic. Although they have different neutron capture properties, the possibility of partial replacement of zirconium by titanium in this kind of alloys was considered in the past. That is why some work has been done on the Sn–Ti–Zr ternary system and published in the past decades [1–3].

The ternary system Sn–Ti–Zr has been scarcely studied. Nowotny et al. [1] observed in 1959 that the Mn_5Si_3-type intermetallic compound can interchange entirely the transition metal elements (from Zr_5Sn_3 to Ti_5Sn_3) in a substitutional way in the same hexagonal structure, i.e. $(Zr, Ti)_5Sn_3$. Glazova and Kurnakov [2] presented in 1961 partial isothermal sections at 500°C, 800°C, 1000°C and 1560°C where hypothetical but controversial phase boundaries were drawn in a confined region of compositions defined by the pure elements Zr and Ti and the binary compound Ti_3Sn. González Camus [3] worked in the Zr-rich composition corner (less than 5 at.% Sn and 10 at.% Ti) with the aim of determining the transformation temperatures from the hcp (α) to the bcc (β) solid solution structures. Finally, the whole isothermal section at 1100°C of the phase diagram of the system based on experimental determinations has been recently published [4].

On the contrary, the binary systems are better known and critical evaluations published recently are accessible: the Sn–Zr system was assessed by Abriata et al. [5] in 1983 and those of the titanium binary systems Ti–Zr [6] and Sn–Ti [7] were published by Murray in 1987. Equilibria in the Sn–Zr system were also experimentally determined by Roberti [8] in 1992 and some modifications were suggested related to the conditions of the invariant transformations of the Zr-rich zone involving the liquid L, the solid solutions α-Zr and β-Zr, and the intermetallics Zr_4Sn and Zr_5Sn_3 proposed in the revision of Abriata et al. [5].

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In 1999, Dupin et al. [9] and Roberti et al. [10] presented calculated phase diagrams of the Sn–Zr system based on different published experimental results. In the Roberti et al. [10] assessment, the formation of the controversial intermetallic compound Zr_5Sn_4 has been considered and added to the equilibrium taking into account the experimental results published in 1990 by Kwon and Corbett [11]. Dupin et al. [9] have omitted this intermetallic in their phase equilibrium calculus.

The purpose of this work is to determine the boundaries of the stable phase domains of the Sn–Ti–Zr ternary system at 900°C via the experimental assessment of the two-phase and three-phase equilibria.

2. Experimental details

Nine alloys were produced by melting the metal components in a non-consumable tungsten electrode arc furnace with a copper crucible and under a high-purity argon atmosphere. Zirconium 99.8 wt% (500–600 ppm Fe, 1000–1100 ppm O), titanium 99.9 wt% (400–500 ppm Fe, 400–500 ppm O) and tin 99.999 wt% were used. The final compositions of the alloys are shown in Table 1.

All specimens were heat treated at (900 ± 2)°C in two periods of 750 h. After each period, the structures of the samples were examined and the compositions of the phases were measured to guarantee the phase equilibria.

In order to perform the heat treatments at the specified temperature, the specimens were wrapped in tantalum foil, encapsulated in quartz tubes under argon atmosphere and placed in a conventional horizontal furnace with a highly accurate temperature control device. The quartz tubes containing the specimens were finally quenched in water at room temperature at the end of the heat treatments.

The different phases were characterized by optical microscopy (Reichert-MEF II), scanning electron microscopy (Philips PSEM-500), energy dispersive spectroscopy (Philips EDX4) and X-ray diffraction (PW3710 Philips). The compositions of the phases were determined by quantitative microanalysis in the electron microprobe (CAMECA SX50).

The specimens were suitably polished and etched. Two different compositions of HNO_3 plus HF water solutions for etching were applied. The 45:5:50 vol% solution was used to reveal the α and β solid solutions and the mixture 20:20:60 vol.% for disclosing the intermetallics. The X-ray diffraction patterns were obtained from fine powders using Cu $K\alpha_1$ and $K\alpha_2$ radiations, adding a monochromator to eliminate the Kβ radiation. The quantitative compositional microanalysis was made in the electron microprobe under an accelerating potential of 20 kV. The equipment was recalibrated before each analysis session using pure 99.99 wt% Zr and Ti and 99.999 wt% Sn standards. The three elements were determined simultaneously.

Table 1
Compositions and phases of alloys

Specimen	Alloy compositions in at.%[a]			Identified phases as-cast [b]	Identified phases at 900°C[b]	Compositions of the equilibrium phases at 900°C in at.%		
	Zr	Ti	Sn			Zr	Ti	Sn
1	69.7	15.1	15.2	β^t	β^t	73.5 ± 0.3	20.3 ± 0.3	6.2 ± 0.2
					$(Zr, Ti)_5Sn_3$	60.4 ± 0.3	2.5 ± 0.2	37.1 ± 0.3
2	56.5	14.8	28.7	$(Zr, Ti)_5Sn_3$	$(Zr, Ti)_5Sn_3$	56.7 ± 0.2	5.8 ± 0.4	37.5 ± 0.3
				β^t	β^t	55.5 ± 0.5	38.7 ± 0.3	5.8 ± 0.2
3	45.5	34.8	19.7	β^t	β^t	38.4 ± 0.3	55.4 ± 0.2	6.2 ± 0.2
				$(Zr, Ti)_5Sn_3$	$(Zr, Ti)_5Sn_3$	53.6 ± 0.3	9.7 ± 0.3	36.7 ± 0.4
4	24.6	54.4	21.0	β^t	β^t	8.9 ± 0.3	81.8 ± 0.4	9.3 ± 0.2
				$(Zr, Ti)_5Sn_3$	$(Zr, Ti)_5Sn_3$	46.8 ± 0.4	16.1 ± 0.4	37.1 ± 0.3
5	8.6	61.9	29.5	Ti_3Sn	Ti_3Sn	0.7 ± 0.2	74.3 ± 0.2	25.0 ± 0.3
				$(Zr, Ti)_5Sn_3$	$(Zr, Ti)_5Sn_3$	19.6 ± 0.3	43.0 ± 0.3	37.4 ± 0.3
6	10.4	74.8	14.8	β^t	β^t	6.4 ± 0.5	84.4 ± 0.5	9.2 ± 0.2
					Ti_3Sn	9.4 ± 0.4	71.3 ± 0.4	19.3 ± 0.3
					$(Zr, Ti)_5Sn_3$	45.8 ± 0.4	17.2 ± 0.3	37.0 ± 0.4
7	2.7	67.0	30.3	Ti_2Sn	Ti_2Sn	2.9 ± 0.3	64.1 ± 0.3	33.0 ± 0.3
				Ti_3Sn	Ti_3Sn	0.2 ± 0.2	74.8 ± 0.2	25.0 ± 0.3
8	9.5	64.1	26.4	Ti_3Sn	Ti_3Sn	4.9 ± 0.4	70.6 ± 0.4	24.5 ± 0.3
				$(Zr, Ti)_5Sn_3$	$(Zr, Ti)_5Sn_3$	39.5 ± 0.6	24.0 ± 0.7	36.5 ± 0.5
9	83.6	5.0	11.4	β^t	α-Zr	88.1 ± 0.4	5.8 ± 0.5	6.1 ± 0.6
					Zr_4Sn	77.0 ± 0.4	3.0 ± 0.3	20.0 ± 0.2

[a] Maximum error in alloy compositions: ±0.1 at.%.
[b] (β^t) stands for the phase characterized as α (hcp) at room temperature which was β (bcc) at the heat treatment temperature.

3. Results and discussion

The phases identified in the as-cast and in the 900°C heat-treated alloys are presented in Table 1. For each specimen, they are ranked in decreasing order according to their relative volume amounts. Results of the composition analysis of the identified equilibrium phases present at 900°C are also compiled in Table 1.

In the following, the bcc solid solution will be referred to as β-(Zr, Ti) taking into account that Zr and Ti atoms can be interchanged in the bcc sites along the whole composition range. On the other hand, the hcp solid solution allows only a limited amount of Ti content in its lattice at 900°C and it will be named α-Zr.

The micrograph of Fig. 1 shows the characteristic Widmannstätten-type structure of the β^t phase [8] in the as-cast alloy No. 9. Specimens of the as-cast alloys Nos. 1, 6 and 9 presented only one phase in the form of large β^t grains. The 900°C isothermal annealing treatment leads to the precipitation of one or two different intermetallic compounds and to the impoverishment of Sn in the solid solution. According to this, the Zr_4Sn compound, precipitated in the α-Zr matrix, is observed in alloy No. 9 (Fig. 2).

Alloys Nos. 2, 3, 4, 5, 7 and 8 exhibited the same phases in the as-cast condition and after the two heat treatment periods at 900°C. Equilibria are assured due to the uniformity of compositions throughout all the phases in every specimen and their structural changelessness during the last period of the heat treatment.

The results obtained from the isothermal treatment of alloy No. 6 were specially used to establish the three-phase equilibrium β-(Zr, Ti) + Ti_3Sn + $(Zr, Ti)_5Sn_3$. The corresponding composition of the phases are

- β-(Zr, Ti): 6.4 at.% Zr–84.4 at.% Ti–9.2 at.% Sn
- Ti_3Sn: 9.4 at.% Zr–71.3 at.% Ti–19.3 at.% Sn
- $(Zr, Ti)_5Sn_3$: 45.8 at.% Zr–17.2 at.% Ti–37.0 at.% Sn

The composition measurements of the phases in the heat-treated specimens of alloy Nos. 5 and 7 show that their total compositions lie both in a two-phase regions (Table 1). One phase (Ti_3Sn) is common to each equilibrium. Moreover, the composition of this intermetallic Ti_3Sn is nearly the same in the two alloys. Those facts allow us to propose a three-phase equilibrium $Ti_3Sn + (Zr, Ti)_5Sn_3 + Ti_2Sn$. The corresponding concentrations of the phases are

- Ti_3Sn: 1 at.% Zr–74 at.% Ti–25 at.% Sn
- $(Zr, Ti)_5Sn_3$: 19.5 at.% Zr–43 at.% Ti–37.5 at.% Sn
- Ti_2Sn: 3 at.% Zr–64 at.% Ti–33 at.% Sn.

The boundaries of the three-phase domains α-Zr + β-(Zr, Ti) + Zr_4Sn and β-(Zr, Ti) + Zr_4Sn + $(Zr,Ti)_5Sn_3$ are drawn after a careful analysis of our own experimental results and those reported by González Camus [3]. The tentative compositions in these equilibria are

- α-Zr: 88 at.% Zr–6 at.% Ti–6 at.% Sn
- β-(Zr, Ti): 83 at.% Zr–12 at.% Ti–5 at.% Sn
- Zr_4Sn: 77 at.% Zr–3 at.% Ti–20 at.% Sn

- β-(Zr, Ti): 78 at.% Zr–16 at.% Ti–6 at.% Sn
- Zr_4Sn: 77 at.% Zr–3 at.% Ti–20 at.% Sn
- $(Zr, Ti)_5Sn_3$: 60.5 at.% Zr–2 at.% Ti–37.5 at.% Sn.

The speculative phase boundaries for the compositional zone containing more than 37.5 at.% Sn are proposed taking into account a critical analysis of the ternary equilibrium results established at 1100°C [4] together with the equilibrium phases present at 900°C in the binary Sn–Zr and Sn–Ti systems. Thus, the two three-phase equilibria involving a Sn-rich liquid L would be the following: L + $ZrSn_2$ + Zr_5Sn_4 and L + Ti_6Sn_5 + Zr_5Sn_4 and the third with only intermetallics could be $(Zr, Ti)_5Sn_3 + Ti_6Sn_5 + Zr_5Sn_4$. The speculative concentrations of each phase are

- L: 9 at.% Zr–4 at.% Ti–87 at.% Sn
- $ZrSn_2$: 30 at.% Zr–3 at.% Ti–67 at.% Sn
- Zr_5Sn_4: 37.5 at.% Zr–18 at.% Ti–44.5 at.% Sn

Fig. 1. Widmannstätten-type structure in as-cast alloy No. 9.

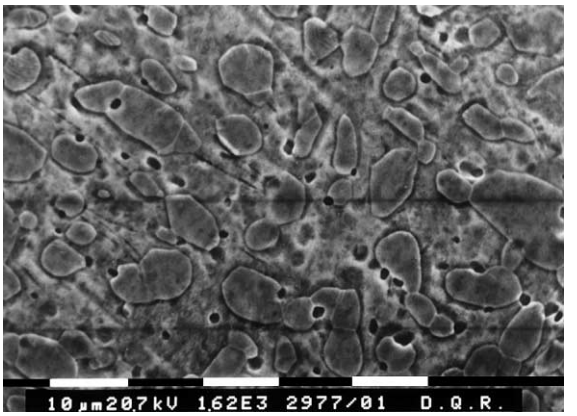

Fig. 2. Two-phase equilibrium after heat treatment at 900°C in alloy No. 9. Precipitation of Zr_4Sn in the α-Zr matrix could be clearly observed.

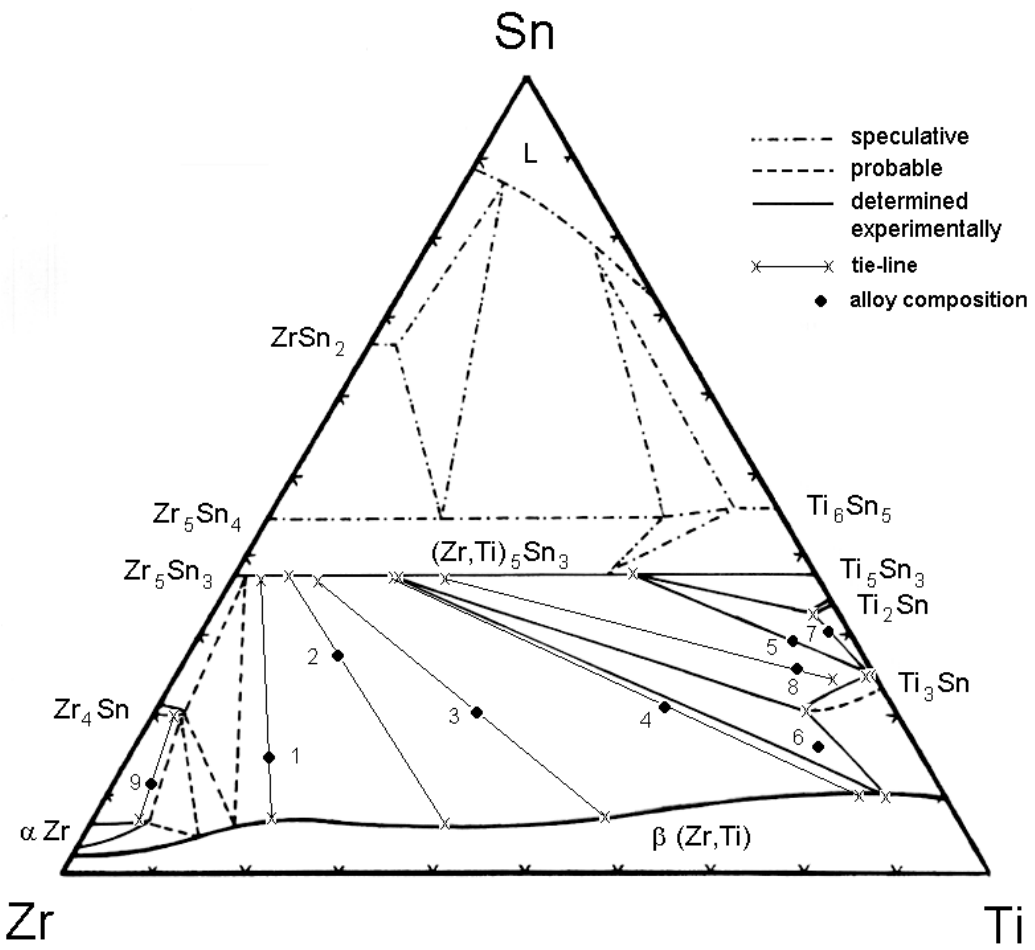

Fig. 3. Isothermal section of the Sn–Ti–Zr system at 900°C, axes in at.%.

- L: 4 at.% Zr–18 at.% Ti–78 at.% Sn
- Ti_6Sn_5: 4.5 at.% Zr–50 at.% Ti–45.5 at.% Sn
- Zr_5Sn_4: 13.5 at.% Zr–42 at.% Ti–44.5 at.% Sn

- $(Zr, Ti)_5Sn_3$: 21.5 at.% Zr–41 at.% Ti–37.5 at.% Sn
- Ti_6Sn_5: 5 at.% Zr–50 at.% Ti–45 at.% Sn
- Zr_5Sn_4: 14 at.% Zr–42 at.% Ti–44 at.% Sn.

Taking into account all the results obtained by the different techniques of analysis employed in this work and the information supplied by previously mentioned works, the whole section of the phase equilibrium diagram at 900°C for the Sn–Ti–Zr system can be drawn. It is shown in Fig. 3.

4. Conclusions

The stable phases which can be found at 900°C in the Sn–Ti–Zr system are the following: Liquid L, α-Zr and β-(Zr, Ti) as solid solutions and Zr_4Sn, Ti_3Sn, Ti_2Sn, $(Zr, Ti)_5Sn_3$ as intermediate compounds.

The two-phase and three-phase equilibria were established for the total range of compositions of the ternary system. Several tie-lines of the two-phase equilibria are given (Table 1). The compositions of the stable phases in the univariant three-phase equilibria are measured or established and reported in the discussion. In the region where the tin composition is higher than 37.5 at.% the extrapolated results from the 1100°C equilibria [4] were taken into account.

The isothermal section at 900°C showing the equilibrium phases of the Sn–Ti–Zr system is presented (Fig. 3). Three kinds of boundaries are drawn taking into account the estimated degree of accuracy: (a) experimentally determined, (b) very probable, (c) speculative.

A considerable dissolution of zirconium in the compounds Ti_3Sn and Ti_6Sn_5 and titanium in Zr_5Sn_4 and a lower amount of zirconium in Ti_2Sn and Ti in Zr_4Sn and $ZrSn_2$ were detected.

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