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Letter to the Editors

A new ternary compound in the Zr–Sn–Fe system

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Abstract

The existence of a ternary compound in the central region of the Zr–Sn–Fe ternary diagram is reported. The compound has been metallographically identified and its composition has been determined by different techniques. The composition obtained at 800°C was: 27.9 ± 0.4 at.% Zr–36.6 ± 0.6 at.% Sn–35.5 ± 0.3 at.% Fe. At 900°C, the resulting composition of the compound was practically the same. The results were used to outline three-phase domains in the tin-rich region of the Zr–Sn–Fe diagram at 800°C and 900°C.

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1. Introduction

Zirconium based alloys are widely employed in the nuclear industry. They are used as cladding and structural material in light and heavy water reactors. Zircaloy-type alloys were developed to obtain materials with good mechanical properties and corrosion resistance, in addition to a low neutron absorption. In the fabrication process of Zircaloys, master alloys of Zr–Sn–Fe are usually used.

Information about the Zr–Sn–Fe system is scarce. Tanner [1] was the first one to report metallographic and X-ray studies of this system. A ternary compound at the composition $Fe_2Sn_3Zr_{11}$ (θ) was first identified by Tanner. However, due to the limitations of the techniques employed and to the lack of a complete knowledge of the Zr–Fe binary phase diagram, he could not recognize the presence of the intermetallics Zr_3Fe and Zr_2Fe in his ternary alloys. Kudriatsev [2] and Korotkova [3] also investigated the same system but they focused mainly in the zirconium-rich region of the diagram. Korotkova confirmed the existence of the θ compound. Corbett [4] studied Zr–Sn alloys with different Fe additions. In the ternary Zr–Sn–Fe phase diagram reported by the Indian Institute of Metals [5] there is no reference to the region studied in this letter.

In the present work the existence of a ternary compound in the central region of the Zr–Sn–Fe ternary diagram is reported. It has been metallographically identified and its composition has been determined by different techniques. The results were used to outline three-phase domains in the tin-rich region of the Zr–Sn–Fe diagram at 800°C and 900°C.

2. Experimental details

The alloy used in this work was of the following composition: 20 at.% Zr–70 at.% Sn–10 at.% Fe. The starting materials were zirconium (99.9% – 600 ppm wt Fe – 200 ppm wt O), tin (99.999%) and iron (99.95%). Buttons (∼ 8 g) were prepared in an arc furnace with a tungsten electrode and a water-cooled copper crucible, in a high purity argon atmosphere (99.999%). The buttons were remelted four times in order to achieve homogeneity. All specimens were heat treated (HT) at 800°C for 680 h, or at 900°C for 432 h. After these treatments the samples were quenched in cold water.

Prior to heat treatments the specimens, carefully cleaned and rinsed, were wrapped in sheets of tantalum

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and sealed in clean silica glass under high purity argon atmosphere.

For the optical and scanning electron microscopy observation, the samples were ground on silicon carbide paper, polished with diamond paste (1/4 μm) and etched with solution reagents in distilled water (H_2O 50%, HNO_3 45%, HF 5%). For the electron microanalysis we used both chemically etched and unetched samples.

Before and after heat treatments, X-ray analyses (PW3710 based Philips) on powdered specimens using monochromatic Cu Kα radiation were performed. Composition analyses were made in an electron microprobe (Cameca SX50) at 20 kV accelerating voltage. Also, semi-quantitative analyses on an X-ray energy dispersive (EDX) spectrometer were performed.

3. Results and discussion

Results from metallographic observation, quantitative electron microprobe analysis and semi-quantitative analysis of EDX reveal the presence of three-phases in the HT samples (Fig. 1(a)): one corresponding to Sn, another to the $ZrSn_2$ compound, and the third one to a new ternary compound, identified in this work as N-phase. This indicates that both samples are in a similar three-phase equilibrium domain at isothermal sections of 800°C and 900°C.

Analyzed by means of the same techniques, the as cast samples (Fig. 1(b)) show the three above mentioned phases and a few grains of a minority phase of composition 38 at.% Zr–45 at.% Sn–17 at.% Fe. Table 1 provides a summary of the composition of the identified phases for the as cast and HT samples. In every case the reported composition was an average of at least 30 individual measurements.

As shown in the table, the N ternary compound presents small differences, not significant, in the Zr and Sn contents between both HT samples. In these samples the Sn phase shows a low solubility of Zr and Fe, which decreases with temperature. Meanwhile, in the as cast sample only traces of these elements are detected. A

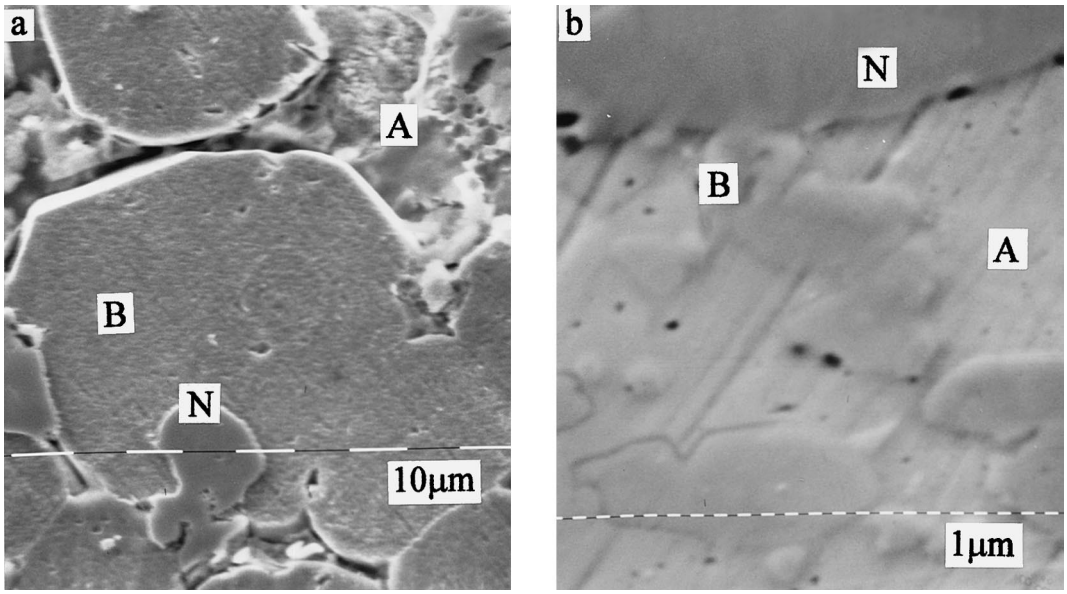

Fig. 1. Scanning electron micrographs of the prepared alloy. (a) 800°C HT and (b) as cast. A: Sn; B: $ZrSn_2$; N: N-phase.

Table 1
Zirconium, tin and iron contents of the identified phases for the as cast and HT samples. ['±' standard deviation ; 0 means less than 0.1]

Identified phases ↓	As cast			800°C–680 h			900°C–432 h		
	at.%			at.%			at.%		
	Zr	Sn	Fe	Zr	Sn	Fe	Zr	Sn	Fe
Sn	0	99.8 ± 0.1	0	0.3 ± 0.1	99.5 ± 0.4	0.2 ± 0.2	0	100 ± 0.1	0
$ZrSn_2$	32.2 ± 0.1	67.0 ± 0.1	0.8 ± 0.1	33.8 ± 0.4	65.7 ± 0.6	0.5 ± 0.2	32.9 ± 0.4	67.1 ± 0.3	0
N-phase	27.2 ± 0.2	37.3 ± 0.2	35.5 ± 0.1	27.9 ± 0.4	36.6 ± 0.6	35.5 ± 0.3	27.3 ± 0.2	37.1 ± 0.2	35.6 ± 0.3

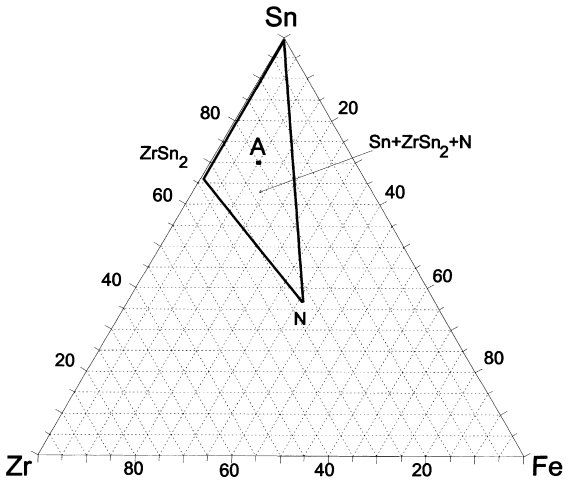

Fig. 2. Zr–Sn–Fe isothermal section at 800°C in at.%. Prepared alloy (A), composition of the three phases obtained after HT, and phase boundaries proposed in this work are only marked.

larger quantity of the N compound in the HT samples than in the as cast one was observed.

Fig. 2 shows the isothermal section at 800°C of the Zr–Sn–Fe system. The initial composition of the alloy prepared, the composition of the three-phases obtained after treatment and considered at equilibrium, and the boundaries for the three-phase domain proposed in this work are marked in this figure. The isothermal section obtained at 900°C is similar.

X-ray diffraction analyses corresponding to the as cast and HT samples show the principal peaks corresponding to Sn and $ZrSn_2$ phases. There are non-identified peaks registered at 2θ equal to 35.1°, 39.1° and 39.7° that would correspond to the N-phase.

4. Conclusions

- A new ternary compound of composition: 27.9 ± 0.4 at.% Zr–36.6 ± 0.6 at.% Sn–35.5 ± 0.3 at.% Fe, at 800°C was found.
- A three-phase equilibrium domain at 800°C in the tin-rich of the Zr–Sn–Fe system was outlined. The equilibrium compositions of the three-phases are practically the same at 900°C.

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