SHORT COMMUNICATION



A Nonconventional Method to Produce Zr Alloys to Study the Fe₂₃Zr₆ Intermetallic Compound in the Fe-Zr System

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Submitted: 29 January 2024/in revised form: 25 September 2024/Accepted: 27 October 2024 © ASM International 2024

Abstract A nonconventional method with an arc furnace was used to produce four binary alloys of Fe79.3Zr20.7 nominal atomic compositions with the aim of studying the Fe₂₃Zr₆ controversial intermetallic compound. The alloys were manufactured with raw materials with different degrees of purity. The existing phases were identified by x-ray diffraction, semi-quantitative microanalysis by means of a scanning electron microscope with an energy dispersive spectrometer attached, and quantitative microanalysis by using an electron microprobe with a wavelength dispersive spectrometer. The Fe₂₃Zr₆ phase, which until now has been observed in grains up to 20 µm in size in arc-furnace samples, was found in millimeter scales in the present work. Moreover, slow cooling of the alloys from the liquid state favors the formation of the Fe₂₃Zr₆ compound, regardless of the degree of purity of the heattreated samples.

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Keywords experimental study · intermetallic compound · iron alloys · metallic alloys · microstructure · non-equilibrium processes · phase diagram

1 Introduction

Zirconium-based alloys are used as cladding for nuclear reactor fuels due to good resistance to corrosion and irradiation damage, adequate mechanical properties and transparency to thermal neutrons. In this sense, the binary phase diagram of the Fe-Zr system has been studied for more than seven decades now by several authors,^[1–5] because understanding the effect of alloying elements on the microstructure will allow tailoring its mechanical properties and properties and prevent potential corrosion effects. However, in the Fe-rich region the stability of the Fe₂₃Zr₆ intermetallic compound remains controversial.

The Fe₂₃Zr₆ phase was first described by Svechnikov and Spektor^[2] as Fe₃Zr compound. Svechnikov *et al.*^[6] noticed that this phase is a line compound whose peritectic reaction temperature is 1482 °C. Kripyakevich *et al.*^[7] found that the crystal structure of this compound corresponds to Mn₂₃Th₆-type. Later, Arias et al.^[8] replaced the Fe₃Zr compound by Fe₂₃Zr₆ in their Fe-Zr phase diagram.

In 2002, experimental work on Fe-Zr systems was published by Stein *et al.*^[9] that highlighted four characteristics of the Fe₂₃Zr₆ phase with the information collected up to that time. (1) *This compound is not always found in the experimental studies.* For example, some authors^[9–20] found this controversial phase but other authors^[21–23] did not report it. However, this could have an explanation if one considers the conclusion of St. John,^[24] that the peritectic reaction is not expected to occur at the peritectic

temperature. Moreover, St. John and Hogan.^[25] classify the Fe₂₃Zr₆ peritectic as C-type, i.e., the least favorable situation for the transformation to occur in their classification, since it is nearly a line compound and it is close to a high temperature eutectic reaction. (2) This phase always occurs only as a third phase in addition to $Fe(\alpha)$ and $Fe_2Zr(C15)$. However, in the last years this compound was found as a second phase in the Cu-Fe-Zr,^[14] Fe-Nb-Zr,^[20] Fe-Hf-Zr^[18] and Fe-Zr^[17-19] systems. (3) It is an oxygen-stabilized phase. It was assumed as a non-stable phase after Stein *et al.*^[9] found a significant increase in oxygen content in the compound by using a qualitative electron probe microanalysis (EPMA) element mapping. However, other researchers^[12,14,17,20] were unable to reproduce this experiment in the Cu-Fe-Zr, Fe-Nb-Zr and Fe-Zr systems, both in diffusion couples^[12,17] and heat-treated samples.^[14,17,20] Furthermore, Zou et al.^[18] and Jiang et al.^[19] recently concluded in their respective researches that the $Fe_{23}Zr_6$ phase is not oxygen-stabilized. (4) The $Fe_{23}Zr_6$ phase is found in small amounts of particles with diameters of 5-10 micrometers, in some cases up to 20 micrometers. It is important to note that this claim has not been refuted so far, because the Fe₂₃Zr₆ compound was found in several experiments, but always in small particles and/or narrow regions.

Regarding this last feature, one of the experimental difficulties to study the physical properties of $Fe_{23}Zr_6$ compound is that regions containing only small grains - were reported: up to 20 µm region widths in arc-furnace samples,^[9,10,13–20,23] whereas in diffusion couple^[12,17] samples these dimensions did not exceed 80 µm. The objective of the present work is to describe a process for fabricating zirconium-based alloys that allows one to obtain larger fractions of $Fe_{23}Zr_6$, thus enabling to study the physical properties of this compound.

2 Experimental

Four alloys of nominal atomic composition Fe_{79.3}Zr_{20.7} (named **T1** to **T4**) were prepared to analyze the phase diagram zone of interest. The raw materials for alloys **T1** and **T2** were zirconium (99.9 wt.%, main impurities being 600 ppm Fe and 200 ppm O) and iron (99.999 wt.%), while for alloys **T3** and **T4**, they were zirconium (99.8 wt.%, main impurities being 800 ppm Fe and 1200 ppm O) and iron (99.95 wt.%). That is to say, two "high" purity (**T1** and **T2**) and two "low" purity alloys (**T3** and **T4**).

Alloy buttons (~ 12 g) were prepared in an arc furnace with a non-consumable tungsten electrode and a watercooled copper crucible, in a high purity argon atmosphere (at least 99.99%). A Cemont SMARTY TX150 welding power supply was used as the current source. To reduce the contamination by oxygen, a Ti-Zr getter was melted prior to the fusion of the samples inside the evacuated chamber. The alloys were then melted four times and turned upside down between successive melts. No significant weight losses were registered.

Finally, the last fusion of the samples was carried out through a nonconventional procedure: the alloys were melted by the electric arc, and then, without interrupting the interaction between the electric arc and the alloys, the intensity of the electric arc current was decreased with a counting time per step of 30 s, during approximately 3 minutes; starting from 115 Amperes (A) downwards, 7 steps of 15 A each. In other words, the alloys were allowed to solidify and cool down while the electric arc was still heating the samples, achieving a slow cooling that lasted several minutes in all cases. In this way, the cooling rate lasted about 5 times longer than the traditional "On-Off" method, in which the electric arc is totally interrupted when the alloys are in the liquid state, and solidification and cooling are produced by uncontrolled heat transfer with the environment. After this process, no significant weight losses were registered in the alloy buttons.

Samples were then heat-treated (HT) at 1200 °C for 10 hours. To accomplish this treatment, they were carefully cleaned, wrapped in tantalum sheets and placed in previously cleaned and dried quartz tubes. For alloys **T1** and **T3**, after achieving a vacuum better than 10^{-4} Pa, the tube was purged with high purity argon and sealed, maintaining the internal argon pressure. In the case of alloys **T2** and **T4**, instead, the vacuum value attained was 10^{-1} Pa; the tube was not purged with argon gas, nor was the internal argon pressure maintained before sealing, *i.e.*, alloys **T2** and **T4** were heat-treated at 10^{-1} Pa in air atmosphere. The aim of this procedure was to manufacture four alloys with different degrees of purity, with sample **T1** being the purest and sample **T4** the least pure.

At the end of the heat treatment, the samples were quenched in a mixture of water and ice without breaking the seal, and then prepared for the quantitative micro-analysis by standard metallographic procedures. In addition, random powder samples were prepared to carry out a structural phase characterization by x-ray diffraction (XRD) in a Philips PW diffractometer equipped with a monochromator. These powders were obtained from the alloy buttons using a diamond file. Measurements were performed in the $20^{\circ} < 2\Theta < 120^{\circ}$ range by using a Cu anode at room temperature.

The existing phases in the heat-treated samples were identified by metallographic techniques (optical microscope Olympus BX-60 M), XRD (PAN Analytical Empyrean diffractometer), scanning electron microscopy analysis with energy dispersive spectrometry (SEM-EDS, JEOL, Thermo and FEI INSPECT S50) and quantitative microanalysis by using an electron microprobe with a wavelength dispersive spectrometer (EPMA-WDS, JEOL JXA8230).

The SEM images were processed with the ImageJ software, and the existing phases were analyzed by applying suitable threshold values, achieving appropriate quantitative estimates for the presence of each phase in each sample.

3 Results

The experimental characterization procedure allowed to observe that the four HT samples (T1 to T4) showed the following three characteristic features, independent of their degree of purity: 1) The presence of the three cubic phases: Fe₂Zr(C15) (Fe with 27.3 at.% Zr), Fe(α) (Fe with 0.6 at.% Zr in solution) and Fe₂₃Zr₆ (Fe with 20.7 at.% Zr). The standard deviation of the EPMA composition measurements was less than 0.3 at.% in all samples. 2) The lattice parameters for the Fe₂Zr(C15), Fe(α) and Fe₂₃Zr₆ phases were $a = (0.7015 \pm 0.0002)$ nm, $a = (0.2866 \pm 0.0002)$ nm and $a = (1.1670 \pm 0.0002)$ nm, respectively. 3) An inhomogeneous structure: the manufacturing method achieved a slow cooling of samples, producing a clear difference in the microstructure between the zone which was always in contact with the electric arc (from the melting to the solidification and cooling processes), henceforth the center zone, and the zone which was always in contact with the water-cooled copper crucible, henceforth the *external zone*. In the present study, the center zone for all HT samples showed a single phase with millimeter lengths. Also, this zone presented pores within the $Fe_{23}Zr_6$ phase in some regions.

Figure 1(a) shows the single $Fe_{23}Zr_6$ phase in the *center* zone for sample T1 HT 1200 °C, whereas Figure 1(b) displays a surface analysis, carried out on a backscattered electron image for this sample, with the relative amount of $Fe_{23}Zr_6$ resulting to be 65.6%. For the sample T1 HT 1200 °C, i.e., the one bearing the highest purity, an EPMA element mapping is shown in Figure 2. In this figure, the bright spots indicate increased element levels. No oxygen was detected in the Fe₂₃Zr₆ compound; however, the oxygen-content detected by EPMA corresponds to the small ZrO₂ region (black colour in Fig. 2d). It is important to notice that the threshold values set for the pores and the small ZrO₂ region were the same as those chosen for the $Fe(\alpha)$ phase. Then, as the relative amount of $Fe(\alpha)$ phase was not exact, the "Fe(α) + ZrO₂ + pores" relative amount value is displayed in Fig. 1(b), corresponding to the black areas in Fig. 1(a).

For a selected *external zone* region of sample **T2** HT 1200 °C, the relative amounts of $Fe_{23}Zr_6$, $Fe_2Zr(C15)$ and "Fe(α) + ZrO₂ + pores" phases were 43.7%, 41.0% and



Fig. 1 (a) Backscattered electron (BSE) image of sample **T1** HT 1200 °C: $Fe(\alpha)$ (black), $Fe_2Zr(C15)$ (grey) and $Fe_{23}Zr_6$ (dark grey). (b) Quantitative surface analysis: 10.6% ($Fe(\alpha) + Zr + pores$) (blue), 23.8% $Fe_2Zr(C15)$ (green) and 65.6% $Fe_{23}Zr_6$ (grey) (Color figure online)

15.3%, respectively, as shown in Fig. 3(d). For the *center* zone, Figure 3(e) (sample **T3** HT 1200 °C) shows 64.3% for the $Fe_{23}Zr_6$ phase, whereas for the sample **T4** HT 1200 °C, the relative amount of $Fe_{23}Zr_6$ phase was 67.7%, as displayed in Fig. 3(f). As an example, Fig. 4 shows the XRD pattern of sample **T4**.

4 Discussion

The Fe₂Zr(C15) + L \rightarrow Fe₂₃Zr₆ peritectic transformation typical microstructure can be appreciated in Fig. 3(a), where the transformation by diffusion during the heat treatment of the Fe₂₃Zr₆ compound that surrounds the Fe₂Zr(C15) phase relies on the slow diffusion of Fe atoms through the Fe₂₃Zr₆ layer to the interface between Fe₂₃Zr₆ and Fe₂Zr(C15) phases.^[4] However, in these intermetallic compounds the corresponding Zr and Fe diffusion coefficients, which govern the growth kinetics of Fe₂₃Zr₆, have been shown to be small.^[4,10,11] This could be another reason, in addition to the one already mentioned,^[24,25] why some authors^[21–23] did not report this compound. Fig. 2 (a, b and c) EPMA element mappings of sample T1 HT 1200 °C for 10 h for (a) oxygen, (b) iron and (c) zirconium. (d) BSE image: ZrO_2 (black), $Fe_2Zr(C15)$ (grey and white, grey) and $Fe_{23}Zr_6$ (dark grey)





Fig. 3 (a) BSE image of sample T2 HT 1200 °C: Fe(α) (black), Fe2Zr(C15) (grey) and Fe23Zr6 (dark grey). (b)BSE image of sample T3 HT 1200 °C: Fe(α) (black), Fe2Zr(C15) (grey) and Fe23Zr6 (dark grey). (c) BSE image of sample T4 HT 1200 °C: Fe(α) (black), Fe2Zr(C15) (grey) and Fe23Zr6 (dark grey).(d) Quantitative surface analysis of a: 15.3% Fe(α) (blue), 41.0% Fe2Zr(C15) (green) and

43.7% Fe23Zr6 (grey). (e) Quantitative surface analysis of **b**: 15.2% (Fe(α) + pores) (blue), 20.5% Fe2Zr(C15) (green) and 64.3 Fe23Zr6 (grey). **f** Quantitative surface analysis of **c**: 17.1% Fe(α) + pores (blue), 18.2% Fe2Zr(C15) (green) and 64.7% Fe23Zr6 (grey) (Color figure online)



Fig. 4 XRD pattern measured in sample T4 HT 1200 °C for 10 h. (A) $Fe(\alpha)$, (B) $Fe_2Zr(C15)$ and (C) $Fe_{23}Zr_6$

According to St John,^[24] the peritectic reaction is unexpected to occur at the peritectic temperature, since adequate cooling is required to create the necessary conditions for nucleation and growth of the peritectic phase to take place. Consequently, the conventional "On-Off" alloy manufacturing method was modified, its aim being to achieve the above-mentioned necessary conditions. Through this procedure the $Fe_{23}Zr_6$ phase, previously found only in small amounts of particles with 3-30 µm lengths,^[4,9] was now present in millimeter lengths in the center zone (Fig. 1a, Fig. 3b and c), which was always in contact with the electric arc. Moreover, Liu et al.,^[4] who manufactured an Fe-10at.% Zr alloy with the traditional method, found less than 4% volume fraction of the Fe₂₃Zr₆ phase in their sample HT at 1190 °C for 48 hours, by using a pixel-counting method similar to the one chosen here. In the present work instead, the volume fraction found was much higher than 4% in all samples (Fig. 1b, Fig. 3d, e and f). It is important to note that these results were found in all the HT samples, independently of the degree of purity of the raw materials, the vacuum value reached before the heat treatment and the gas atmosphere used for it. Therefore, less impurities appear not to be so decisive in the formation of the Fe23Zr6 peritectic phase, which was one of the two suggestions by Yang et al.^[15] On the contrary, the slow cooling during solidification has proven to be clearly more decisive than impurities.

The oxygen-content detected in the sample **T1** (Fig. 2) in the Fe₂₃Zr₆ compound was not higher than in the Fe₂. Zr(C15) phase, in agreement with Ewh,^[12] Huang *et al.*,^[14] Du *et al.*^[17] and Tolosa *et al.*^[20] but in disagreement with Stein *et al.*^[9] Moreover, Jian *et al.*^[19] concluded that the Fe₂₃Zr₆ phase is not oxygen stabilized because oxygen has no effects on its formation under different heat treatment atmospheres. The same was observed in the present work. Abraham *et al.*^[11] found a Zr-rich region (<5at.% Fe)

within Fe₂₃Zr₆. This was explained by Zou *et al.*,^[18] based on their own results and those by Wei *et al.*,^[26] considering the depletion of the Fe during the diffusion between Fe₂₃. Zr₆ and Fe₂Zr, resulting in the generation of Fe vacancies. These vacancies of Fe, which have been proven to have a strong oxygen absorption ability,^[19] could explain the reason why ZrO₂ was found inside of Fe₂₃Zr₆ compound in Fig. 2. Furthermore, this controversial peritectic phase was not reported in the Fe-O-Zr phase diagram.^[27,28]

5 Conclusions

The controversial $Fe_{23}Zr_6$ phase was re-examined on Fe-Zr binary alloys heat-treated at 1200 °C. These samples were produced with raw materials of different degrees of purity by using a nonconventional manufacturing method that led to produce the $Fe_{23}Zr_6$ compound on millimeter scales. The results obtained suggest that cooling the alloys slowly from the liquid state favors the formation of the $Fe_{23}Zr_6$ compound, independently of the degree of purity of the HT samples.

Acknowledgment This work was supported by a CONICET Scholarship and Research Council of the Universidad Nacional de Tucumán (CIUNT) through Project PIUNT E735. The authors acknowledge the assistance of to Dr. Germán Bridoux (LAFISO-INFINOA, UNT-CONICET), and Dr. Gladys Nieva and Dr. Julio Guimpel (Centro Atómico Bariloche, CNEA) at different stages of the current investigation.

Data Availability The raw/processed data required to reproduce these findings cannot be shared at this time as the data also form part of an ongoing study.

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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