

Short communication on experimental phase diagram of the Fe corner in the Fe–Nb–Zr system at 800 °C

C. Arreguez ^a, M.R. Tolosa ^{a,*}, D. Arias ^b, C. Corvalán ^c, N. Nieva ^a

^a Laboratorio de Física del Sólido, Instituto de Física del Noroeste Argentino (INFNOA), Departamento de Física, Facultad de Ciencias Exactas y Tecnología, Universidad Nacional de Tucumán (UNT), Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Argentina

^b Instituto de Tecnología J. Sabato, Comisión Nacional de Energía Atómica Argentina, Universidad Nacional de San Martín, Buenos Aires, Argentina

^c Gerencia de Materiales, Comisión Nacional de Energía Atómica Argentina (CNEA), Universidad Nacional de Tres de Febrero, Argentina, CONICET, Consejo Nacional de Investigaciones Científicas y Técnicas, Argentina

ARTICLE INFO

Article history:

Received 15 March 2018

Received in revised form

18 June 2018

Accepted 21 June 2018

Available online 22 June 2018

ABSTRACT

Phase diagram in the Fe corner of the Fe–Nb–Zr system at 800 °C was determined by X-ray diffraction (XRD) and quantitative microanalysis by using electron microprobe with wavelength dispersive spectrometry (SEM-WDS). The existence of two three-phase fields ($C36(Zr_{1-x}Nb_x)Fe_2 + Fe(\alpha) + C15$) and ($C36(Zr_{1-x}Nb_x)Fe_2 + Fe(\alpha) + C14$) and three two-phase fields ($C36(Zr_{1-x}Nb_x)Fe_2 + Fe(\alpha)$), ($Fe(\alpha) + C14$) and ($Fe(\alpha) + C15$) are proposed in the present work.

© 2018 Elsevier B.V. All rights reserved.

1. Short communication

Zirconium based alloys are widely used as fuel cladding in nuclear pressurized water reactors for their excellent mechanical properties, irradiation stability and resistance to corrosion. To meet the requirements of higher burnup of the nuclear fuel, a new generation of Nb containing zirconium-based alloys, such as Zirlo[®] [1–3], M5[®], E110[®] and E635[®] [3,4] was developed. A greater knowledge of the effect of the alloying elements will allow advancing in the understanding of their microstructure; mechanical properties and corrosion depend strongly on it.

The information on the ternary phase diagrams of the main components of the Zirlo type alloys (Fe–Sn–Zr, Fe–Nb–Sn and Fe–Nb–Zr) is still incomplete and, according to many authors, some uncertainties persist. A systematic study should include the study of all binary, ternary and even quaternary systems of these metallurgical systems at different temperatures.

One of the first experimental studies on the Fe–Nb–Zr phase diagram system was performed by Gruzdeva et al. [5] in 1968. They focused on the Zr corner in Gibbs triangles regarding these phase diagrams at 700, 800, 900 and 1000 °C. In 1989, Korotkova and Alekseeva [6,7] proposed seven isothermal sections along the

temperature range from 850 to 1600 °C [6] and from 500 to 800 °C [7] spanning the whole composition range, except for the Fe-rich corner. Later on, Korotkova [8] presented two isothermal sections in the Fe–Fe₂Zr–Fe₂Nb region at 1315 and 1337 °C.

Between 1990 and 2008, several authors researched this system in different areas at several isothermal sections [9–23] but they did not study the Fe-rich corner adjacent area.

In 2013, Tang et al. [24] studied the system at 1200 °C. Among other results, they found the compound Fe₂₃Zr₆ in the iron-rich alloys they used. This compound was described for the first time in 1962 by Svechnikov et al. [25,26] and to date, its existence remains controversial.

In 2015, Liang et al. [27] studied the system experimentally at 700 °C and, like Tang et al. [24], they also found the compound Fe₂₃Zr₆ in iron-rich alloys.

In 1969, Kanematsu et al. [28] reported that the crystal structure of (Zr_{1-x}Nb_x)Fe₂ phase is MgCu₂(C15) type for $x \leq 0.3$, MgNi₂, holding (C36) structure type for $0.35 < x < 0.5$ and MgZn₂ being (C14) structure type for $x > 0.5$. For the (Zr_{1-x}Nb_x)Fe₂ phase, the six-layer structure has a MgNi₂ structure, which has similar X-ray patterns to MgZn₂ type. Hence, both Tang [24] and Liang [27] concluded that it is hard to differentiate MgNi₂ from MgZn₂ structure type by using XRD techniques.

As was previously mentioned, there is scarce experimental information on the Fe–Nb–Zr ternary system in the Fe-rich corner. The present work deals with the experimental phase diagram of this region in the Fe–Nb–Zr system at 800 °C.

* Corresponding author.

E-mail addresses: tolosamartinr@gmail.com (M.R. Tolosa), nnieva@herrera.unt.edu.ar (N. Nieva).

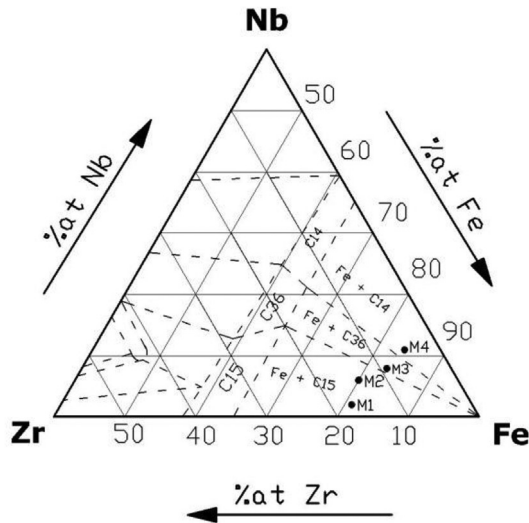


Fig. 1. Zr-rich corner of system Fe-Nb-Zr. Tentative isothermal section proposed by Raghavan [16] at 800 °C (dotted lines). The compositions synthesized in the present work are shown as small black circles.

For the experiments, four ternary alloys were designed to analyze the area of interest. They were melted and submitted to heat treatments at 800 °C for 3720 h. The raw materials were zirconium (99.9 wt %), niobium (99.98 wt %) and iron (99.95 wt %). Buttons (~7 g) were prepared in an arc furnace with a non-consumable tungsten electrode and a water-cooled copper crucible, in a high purity argon atmosphere (99.999%). To reduce the contamination of oxygen, a Zr-Ti getter was melted prior to melting. The alloys were melted at least four times and turned upside down between each melting. No significant weight losses were registered. The samples were carefully cleaned, wrapped in tantalum sheets and placed in a silica glass tube previously cleaned and dried. The tube was purged with high purity argon gas and sealed, keeping internal pressure of Ar. At the end of the heat treatment, the samples were quenched in water without breaking the seal.

After the heat treatments, the samples were prepared for characterization. For the quantitative microanalysis, samples were ground with silicon carbide paper and polished with a cloth and diamond paste down to a particle size of 0.25 μm. Random powder samples were prepared to carry out a phase-structural characterization of the alloys by an X-ray diffraction (XRD) analysis. X-ray patterns were obtained with a Philips PW diffractometer equipped with a monochromator. Measurements were performed in the 10°–120° 2θ range using a Cu anode at room temperature.

Table 1

Nominal compositions of the alloys, characterization of the samples: phase identification, chemical composition (SEM-WDS), structure type and lattice parameters (XRD) in the 800 °C HT samples. When calculating was possible, the standard deviation of compositions was less than 0.3 at%.

Samples	Nominal composition [at%]	Phases	Phase compositions [at%]	Structure type [Å]	Lattice parameters
M1	Fe ₈₁ Nb ₂ Zr ₁₇	Fe(α)	Fe _{98.7} Nb _{0.6} Zr _{0.7}	W	a = 2.8699
		C15	Fe _{71.4} Nb _{2.0} Zr _{26.6}	Cu ₂ Mg	a = 7.0155
M2	Fe ₈₀ Nb ₆ Zr ₁₄	C36(Zr _{1-x} Nb _x)Fe ₂	Fe _{72.4} Nb _{13.7} Zr _{13.9}	Ni ₂ Mg	a = 4.9363 c = 16.1509
		Fe(α)	Fe _{98.8} Nb _{0.5} Zr _{0.7}	W	a = 2.8724
		C15	Fe _{71.4} Nb _{6.0} Zr _{22.6}	Cu ₂ Mg	a = 7.0101
M3	Fe ₈₃ Nb ₈ Zr ₉	C36(Zr _{1-x} Nb _x)Fe ₂	Fe _{72.3} Nb _{12.7} Zr _{15.0}	Ni ₂ Mg	a = 4.9146 c = 16.0393
		Fe(α)	Fe _{98.5} Nb _{0.8} Zr _{0.7}	W	a = 2.8656
		C15	Fe _{71.5} Nb _{3.9} Zr _{24.6}	Cu ₂ Mg	a = 6.9247
M4	Fe ₈₄ Nb ₁₁ Zr ₅	C36(Zr _{1-x} Nb _x)Fe ₂	Fe _{72.5} Nb _{14.7} Zr _{12.8}	Ni ₂ Mg	a = 4.8610 c = 15.9770
		Fe(α)	Fe _{98.0} Nb _{1.0} Zr _{1.0}	W	n.d.
		C36(Zr _{1-x} Nb _x)Fe ₂	Fe _{71.8} Nb _{18.7} Zr _{9.5}	Ni ₂ Mg	
		C14(Fe ₂ Nb)	Fe _{69.8} Nb _{24.2} Zr _{6.0}	MgZn ₂	

n.d.: Not determinate.

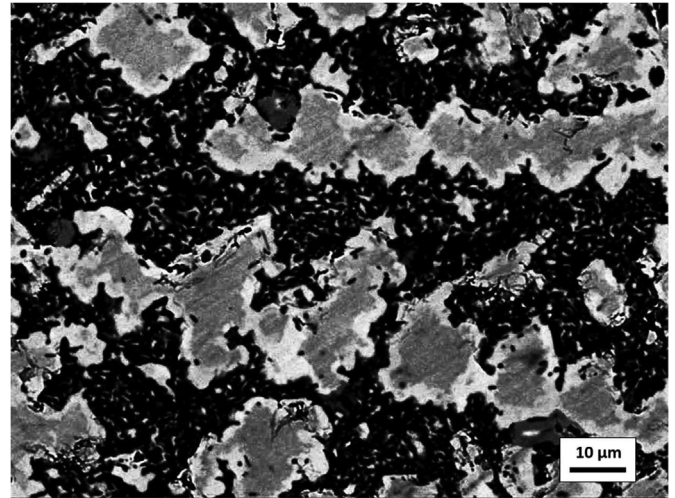


Fig. 2. Back scattered electron SEM images of sample M1: Fe (dark), C15 (dark grey) and C36 (grey).

The present phases in heat-treated samples were identified by metallographic techniques (optical microscope Olympus BX-60 M), X-ray diffraction (XRD, PAN Analytical Empyrean diffractometer) and quantitative microanalysis by using an electron microprobe with a wavelength dispersive spectrometry (SEM-WDS, JEOL JXA-8230).

The chemical composition of each sample is indicated in Fig. 1. It shows the above mentioned compositions in a portion of the phase diagram corresponding to the Fe corner, in which the phase boundaries proposed by Raghavan [16] have been delineated.

A summary of the characterization results is shown in Table 1. The nominal composition of alloys labeled as M1 to M4 is shown. Also, the identified phases with crystal structure and chemical compositions of the samples heat-treated (HT) at 800 °C are indicated. Crystal structure was obtained from the results of XRD and the chemical compositions of SEM-WDS measurements. Fig. 2 shows a typical microstructure of sample M1.

In the case of alloy M4, it was not possible to find the lattice parameters by using XRD because of two reasons, namely, the low amount of C14 phase and the fact that the main diffraction peaks overlay between C14 and C36 phases. As stated before, and in accordance with Kanematsu et al. [28], the structure of MgNi₂ and MgZn₂ types have similar X-ray patterns. Thus, it is hard to see the difference between them by using XRD techniques. However, using SEM-WDS allowed separating and measuring them. As shown in

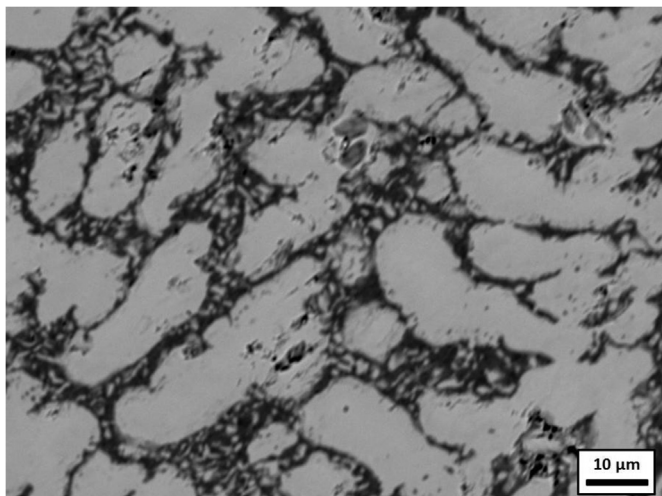


Fig. 3. Back scattered electron SEM images of sample M4: Fe (dark), C14 (dark grey) and C36 (grey).

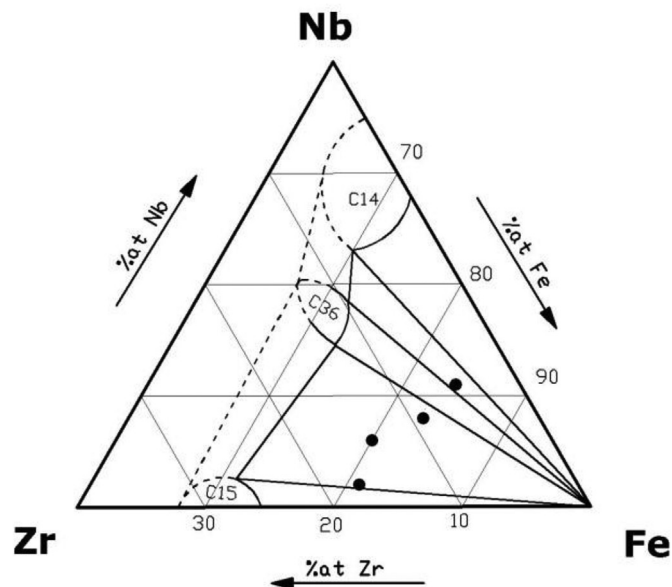


Fig. 4. Phase diagram of Fe-Nb-Zr proposed at 800 °C Fe-rich corner. (•) Nominal alloy compositions. Limits of phases: thick lines measured in the present work, (– –) probable.

Fig. 3, three phases were found.

The results obtained differ from those proposed by Raghavan et al. [16]. In the Fe-rich area, Raghavan proposes three schematic two-phase zones (C14 + Fe(α)), (C15 + Fe(α)) and (C36 + Fe(α)) as shown in Fig. 1. In the Fe-rich area we found the existence of two three-phase fields (C36(Zr_{1-x}Nb_x)Fe₂ + Fe(α) + C15) and (C36(Zr_{1-x}Nb_x)Fe₂ + Fe(α) + C14) and the existence of three two-phase fields (C36(Zr_{1-x}Nb_x)Fe₂ + Fe(α)), (Fe(α) + C14) and (Fe(α) + C15).

Results of the present work at 800 °C resemble those proposed by Liang et al. [27] at 700 °C. The main discrepancy is related to the homogeneity domain of phases C14, C15 and C36. The Fe₂₃Zr₆ phase was not found.

Finally, by using the results of characterization of HT alloys for long annealing times and the preliminary results published in previous works [14,16,27,29,30], a phase diagram section at 800 °C

in the Fe rich corner of the Fe–Nb–Zr system has been constructed, as shown in Fig. 4.

Acknowledgments

This work was supported by the Research Council of the National University of Tucuman (CIUNT) through Project PIUNT26/E433. The authors are thankful to Dr. Nicolás Di Lalla and Dr. Daniel Vega (Constituyentes Atomic Center, CNEA) and Dr. Gustavo Castellano (LAMARX, FaMAF, UN Córdoba).

References

- [1] G.P. Sabol, G.R. Kile, M.G. Bafour, E. Roberts, Development of a cladding alloy for high burnup, in: Proceedings 8th International Symposium on Zirconium in the Nuclear Industry, ASTM STP, Philadelphia, 1989, p. 227.
- [2] K.T. Erwin, O. Delaire, A.T. Motta, Y.S. Chu, D.C. Mancini, R.C. Birtcher, Observation of second-phase particles in bulk zirconium alloys using synchrotron radiation, *J. Nucl. Mater.* 294 (2001) 299–304.
- [3] A.V. Nikulina, Metal materials for the elements of nuclear reactors, *Met. Sci. Heat. Treat.* 45 (2003) 292.
- [4] J.P. Mardon, D. Charquet, J. Senevat, Influence of composition and fabrication process on out-of-pile and in-pile properties of M5 Alloy, in: Proceedings 12th International Symposium on Zirconium in the Nuclear Industry, ASTM STP, West Conshohocken, 2000, p. 505.
- [5] N.M. Gruzdeva, T.N. Zagorskaya, I.N. Raevskii, Zirconium Corner of the Zr–Nb–Fe Phase Diagram, *Physical Chemistry of Zirconium Alloys* (in Russian), Academy of Sciences USSR, Moscow, 1968, p. 117.
- [6] Z.M. Alekseeva, N.V. Korotkova, Isothermal sections of state diagram of Zr–Nb–Fe in the temperature range 1600–850 °C, *Izv. Akad. Nauk. SSSR Met.* 1 (1989) 199 in Russian; TR: *Russ. Metallurgy*, 1 (1989) 203.
- [7] N.V. Korotkova, Z.M. Alekseeva, Topology of the Zr–Nb–Fe phase diagram in the range 500–800 °C, *Izv. Akad. Nauk. SSSR Met.* 3 (1989) 207 in Russian; TR: *Russ. Metallurgy*, 3 (1989) 198.
- [8] N.V. Korotkova, The Fe–ZrFe₂–NbFe₂ phase diagram, *Izv. Akad. Nauk. SSSR Met.* 6 (1989) 194 in Russian; TR: *Russ. Metallurgy*, 6 (1989) 195.
- [9] O.T. Woo, G.J.C. Carpenter, Microanalytical identification of a new Zr–Nb–Fe phase, in: L.D. Peachey, D.B. Williams (Eds.), *Proceeding of 12th International Congress for Electron Microscopy*, San Francisco Press, Seattle, Washington, 1990, p. 132.
- [10] V. Raghavan (Ed.), *Phase Diagrams of Ternary Fe Alloys*, Part 6b, 248, Indian Institute of Metals, Calcutta, 1992, p. 1031.
- [11] V.A. Markelov, V.Z. Ratikov, S.A. Nikulin, V.I. Goncharov, V.N. Shishov, A.Yu. Gusev, E.K. Chesnokov, *Phys. Met. Metallogr.* 77 (1994) 380.
- [12] V.N. Shishov, A.V. Nikulina, V.A. Markelov, M.M. Perehud, A. Kozlov, S. Averin, S. Kolbenkov, A. Novoselov, in: *Proceedings of the 11th Int. Symp. on Zr in the Nuclear Industry*, 1295, ASTM STP, 1996, p. 603.
- [13] A.V. Nikulina, V.A. Markelov, M.M. Perehud, V.N. Voevodin, V.L. Panchenko, G.P. Kobylansky, Irradiation-induced microstructural changes in Zr–1 % Sn–1 % Nb–0.4 % Fe, *J. Nucl. Mater.* 238 (1996) 205.
- [14] M.S. Granovsky, M. Canay, E. Lena, D. Arias, Experimental investigation of the Zr corner of the ternary Zr–Nb–Fe phase diagram, *J. Nucl. Mater.* 302 (2002) 1.
- [15] C. Toffolon-Masclat, J.C. Brachet, G. Jago, Studies of second phase particles in different zirconium alloys using extractive carbon replica and an electrolytic anodic dissolution procedure, *J. Nucl. Mater.* 305 (2002) 224.
- [16] V. Raghavan, Fe–Nb–Zr (Iron–Niobium–Zirconium), *J. Phase Equil.* 24 (4) (2003) 354.
- [17] P. Barberis, D. Charquet, V. Rebeyrolle, Ternary Zr–Nb–Fe(O) system: phase diagram at 853 K and corrosion behavior in the domain Nb < 0.8 %, *J. Nucl. Mater.* 326 (2004) 163.
- [18] V.N. Shishov, M.M. Perehud, A.V. Nikulina, Y.V. Pimenov, G.P. Kobylansky, A.E. Novoselov, Z.E. Ostrovsky, A.V. Obukhov, Influence of structure -Phase state of Nb containing Zr alloys on irradiation-induced growth, *J. ASTM Int.* 2 (2005). JAI12431.
- [19] H.G. Kim, J.Y. Park, Y.H. Jeong, Ex-reactor corrosion and oxide characteristics of Zr–Nb–Fe alloys with the Nb/Fe ratio, *J. Nucl. Mater.* 347 (2005) 140.
- [20] C. Toffolon-Masclat, P. Barberis, J.-C. Brachet, J.-P. Mardon, L. Legras, Study of Nb and Fe precipitation in a-phase temperature range (400 to 550 °C) in Zr–Nb(Fe–Sn) alloys, *J. ASTM Int.* 2 (2005). JAI12321.
- [21] C. Ramos, C. Saragovi, M.S. Granovsky, Some new experimental results on the Zr–Nb–Fe system, *J. Nucl. Mater.* 366 (2007) 198.
- [22] C. Toffolon-Masclat, T. Guilbert, J.C. Brachet, Study of secondary intermetallic phase precipitation/dissolution in Zr alloys by high temperature: high sensitivity calorimetry, *J. Nucl. Mater.* 372 (2008) 367.
- [23] C. Toffolon-Masclat, J.C. Brachet, C. Servant, J.M. Joubert, P. Barberis, N. Dupin, P. Zeller, Contribution of thermodynamic calculations to metallurgical studies of multi-component zirconium based alloys, *J. ASTM Int.* 5 (2008). JAI10122.
- [24] Y. Tang, C. Liao, J. Meng, J. Zhu, Q. Zhu, L. Nong, J. Liang, Phase equilibria in the

- Fe-Nb-Zr ternary system at 1200°C, *Rare Met.* 32 (2013) 201.
- [25] V.N. Svechnikov, A.Ts Spektor, The iron-zirconium phase diagram, *Proc. Acad. Sci. USSR, Chem. Sect* 142 (1962) 231 (in English; TR: *Dokl. Akad. Nauk. SSSR*, 143 (1962) 613.
- [26] V.N. Svechnikov, V.M. Pan, A.Ts Spektor, Intermediate phases in the iron-zirconium system, *Russ. J. Inorg. Chem.* 8 (1963) 1106 (in English; TR: *Zh. Neorg. Khim.*, 8 (1963) 2118.
- [27] J. Liang, M. Zhang, Y. Ouyang, G. Yuan, J. Zhu, J. Shen, M.R. Daymond, Contribution on the phase equilibria in Zr-Nb-Fe system, *J. Nucl. Mater.* 466 (2015) 627.
- [28] K. Kanematsu, Structural and magnetic properties of pseudo binary system $(Zr_{1-x}Nb_x)Fe_2$, *J. Phys. Soc. Jpn.* 27 (1969) 849.
- [29] S. Voß, M. Palm, F. Stein, D. Raabeu, Phase equilibria in the Fe-Nb system, *J. Phase Equilibria Diffusion* 32 (2) (2011) 97.
- [30] F. Stein, G. Sauthoff, M. Palm, Experimental determination of intermetallic phases, phase equilibria, and invariant reaction temperatures in the Fe-Zr system, *J. Phase Equilibria Diffusion* 23 (6) (2002) 480.