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Mössbauer spectroscopy characterization of Zr–Nb–Fe phases

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Abstract

The aim of this work was the characterization of the ternary phases and of those coming from the corresponding binary systems in the Zr–Nb–Fe diagram by means of Mössbauer spectroscopy. This is part of a complete study involving a tentative isothermal section at 900 °C of the center of the Zr–Nb–Fe diagram which will be published elsewhere.

Zr–Nb–Fe alloys with Nb contents between 5 and 50 at% and Fe contents between 10 and 60 at% were analyzed after a heat treatment at 900 °C for 4 month. Mössbauer characterization of the phases was complemented by optical and scanning electron microscopies, X-ray diffraction and electron microprobe analysis.

From the obtained results it can be inferred that Fe in both of the Laves phases present in this system ($Zr(FeNb)_2$ and $(ZrNb)Fe_2$) sees different environments, producing quadrupole splitting and hyperfine field distributions, respectively. Two types of body centered cubic β phases (Zr-rich and Nb-rich) were found having noticeable differences in their Mössbauer parameters. Furthermore it was shown that the ternary $Fe(NbZr)_2$ compound would show magnetic character at low temperatures. Concentration dependence of the hyperfine parameters and their relations with the lattice parameters contributed to the structural characterization of the phases.

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Keywords: Mössbauer spectroscopy; Zr-based alloys; Laves phases; Ternary systems

1. Introduction

Zr alloys are widely used as corrosion-resistant materials in chemical process industrial equipments and in nuclear power reactors fuel elements due to their noble properties at high temperature, in particular good mechanical and radiation damage resistance and low thermal neutron capture cross-section.

The corrosion properties and the strength of Zr can be improved by alloying it with transition metals. That is the case of Zirlo (Zr–1%Nb–1%Sn–0.1%Fe–0.1%O), alloy which present Zr–Nb–Fe precipitates. It is then necessary to study the ternary phase diagram corresponding to those precipitates.

Using Mössbauer spectroscopy complemented by optical and scanning electron microscopies, X-ray diffraction (XRD) and electron microprobe analysis, the ternary phases and those coming from the corresponding binary systems in the Zr–Nb–Fe diagram were characterized. For that purpose Zr–Nb–Fe alloys with Nb contents between 5 and 50 at% and Fe contents between 10 and 60 at% were studied after a heat treatment at 900 °C for 4 month.

Mössbauer spectroscopy is not a commonly used technique in these kind of works, however our results and previous studies [1–3] demonstrates that it gives very useful information, sometimes not provided by other techniques. Its sensitivity to small changes in the surroundings of the probe atom, ^{57}Fe in this case, makes possible the hyperfine interactions between the nucleus and the electrons density to be measured, giving information about the local crystal symmetry and the magnetic and electronic properties around the iron nuclei. Mössbauer spectroscopy in phase analysis can distinguish between the different phases present in the alloy by the variation of at least one of the hyperfine parameters. This technique has the

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advantage that it requires only relatively small quantities of the samples, detecting iron-rich phases at quantities less than 0.5 at%.

2. Experimental

Button-shaped alloys were prepared from pure elements, 99.9 wt% Fe, 99.8 wt% Zr and Nb and Zr–20%Nb with Fe impurities less than 500 ppm and O impurities less than 1200 ppm. They were melted in an argon arc furnace and then wrapped in Ta foils and sealed in quartz tubes under a high-purity argon atmosphere to perform annealing at 900 °C for 4 month. Each button was finally cut, polished and chemically etched with suitable mixes of acids.

Nominal chemical compositions of the alloy samples are: $Zr_{30}Nb_5Fe_{65}$, $Zr_{45}Nb_{10}Fe_{45}$, $Zr_{40}Nb_{20}Fe_{40}$, $Zr_{40}Nb_{30}Fe_{30}$, $Zr_{40}Nb_{40}Fe_{20}$, $Zr_{40}Nb_{50}Fe_{10}$ and $Zr_{61}Nb_{30}Fe_9$.

Metallographies were taken using both, an optical microscope and a Philips scanning electron microscope.

The composition of the phases present in the alloy samples was determined using a Cameca SX50 electron probe microanalyzer.

The absorbers for XRD and Mössbauer studies were obtained using a diamond file to avoid Fe impurities. Powder quantities for Mössbauer analysis were calculated taking into account the thin absorber approximation.

XRD patterns were obtained with the Kα radiation of a Cu tube ($\lambda = 1.5418$ Å). Data were analyzed by the Rietveld Refinement Structure program [4].

Constant acceleration Mössbauer spectra were collected by means of a standard multichannel transmission spectrometer with a ^{57}Co source in Rh matrix. Each run was made at room temperature (RT), just in one case ($Zr_{40}Nb_{40}Fe_{20}$ sample) the spectrum was also run at 15 K. Spectra were fitted using the NORMOS program [5], considering sodium nitroprusside as standard.

3. Results

Combining Mössbauer spectroscopy results with XRD, optical and scanning electron microscopies and microprobe analysis it can be inferred that in addition to both Laves phases ((Zr(FeNb)$_2$ and (ZrNb)Fe$_2$)) present in this system there are two types of body centered cubic β phases (Zr-rich and Nb-rich) and a ternary Fe(NbZr)$_2$ compound. From now on the Fe(NbZr)$_2$ and (Zr(FeNb)$_2$ phases will be referred to as λ_1 and λ_2 respectively.

Mössbauer parameters are displayed in Table 1 and the corresponding spectra are shown in Fig. 1. For the Laves phases quadrupole splitting (QS) and hyperfine field (HF) values correspond to the average of the distribution and isomer shift (IS) values are the most probable values. Fig. 2 displays the QS distributions for the λ_2 phase in the $Zr_{40}Nb_{30}Fe_{30}$ and the $Zr_{40}Nb_{50}Fe_{10}$ samples and Fig. 3 shows the HF distribution for (ZrNb)Fe$_2$ in the $Zr_{30}Nb_5Fe_{65}$ sample.

Table 1
Mössbauer parameters

Sample	IS (mm/s)	QS (mm/s)	HF (T)	Phase
$Zr_{45}Nb_{10}Fe_{45}$	−0.16	0.30	—	λ_1
	−0.19	0.27	—	λ_2
$Zr_{40}Nb_{20}Fe_{40}$	−0.14	0.25	—	λ_1
	−0.25	0.27	—	λ_2
$Zr_{40}Nb_{30}Fe_{30}$	−0.19	0.23	—	λ_1
	−0.29	0.45	—	λ_2
	−0.12	0.28	—	βZr
$Zr_{40}Nb_{40}Fe_{20}$	−0.30	0.45	—	λ_2
	−0.10	0.28	—	βZr
	−0.18	0.22	—	βNb
$Zr_{40}Nb_{50}Fe_{10}$	−0.30	0.51	—	λ_2
	−0.09	0.27	—	βZr
	−0.20	0.24	—	βNb
$Zr_{61}Nb_{30}Fe_9$	−0.29	0.50	—	λ_2
	−0.13	0.26	—	βZr
$Zr_{30}Nb_5Fe_{65}$	−0.18	0.30	—	λ_2
	−0.13	0.00	16	(ZrNb)Fe$_2$

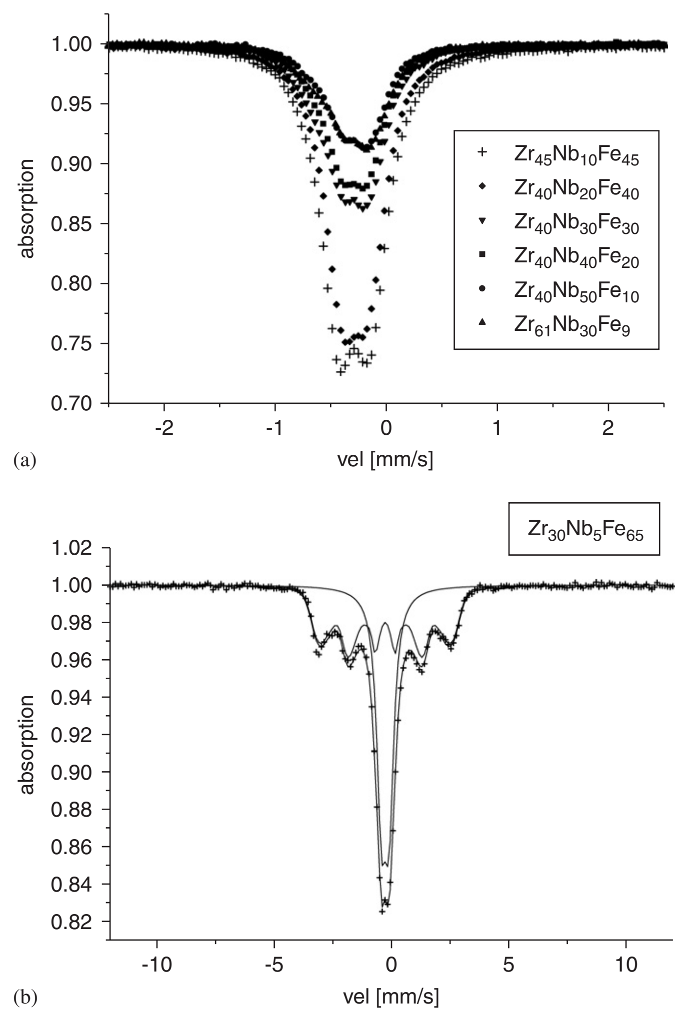

Fig. 1. Mössbauer spectra at RT for the samples with paramagnetic phases (a) and fitted spectrum for the $Zr_{30}Nb_5Fe_{65}$, the only sample with a magnetic phase (b).