

Investigations of redistribution of iron in a zirconium alloy due to neutron irradiation

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Abstract Data were obtained with the help of ^{57}Fe Mössbauer spectroscopy about the redistribution of iron atoms between intermetallic precipitates and between precipitates and the solid solution phase in E635-type alloy (Zr-1.2 wt% Sn-0.34 wt% Fe-1.0 wt %Nb-0.03–0.05 wt% O) due to neutron irradiation.

Keywords Mossbauer effect · Zirconium alloys · Neutron irradiation

1 Introduction

The main problem of nuclear power at the present is the safety of the utilization of nuclear reactor operation with increased duration of their use and, as a result, more profound fuel burnup. In solving this problem it is important to increase the corrosion and radiation resistance of the alloys used in the reactors. As structural elements in the active zone of reactors subjected to thermal neutrons alloys on the basis of zirconium are used. Establishing a relationship between the transformations due to radiation and the initial composition of these alloys gives the possibility to modify existing alloys with a view to improving their basic properties [1, 2]. Important information about the origin and the evolution of secondary phases and about the redistribution in alloys used as matrix elements in the course of thermo-mechanical processing, as well as information about the radiation phase transformations under reactor irradiation can be obtained with the help of Mössbauer spectroscopy, when Mössbauer-active elements (iron and tin) are constituents of the alloys [2].

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2 Experimental set-up and performance

The alloy E635 (Zr-1.2 wt% Sn-0.34 wt% Fe-1.0 wt %Nb-0.03–0.05 wt% O) was selected for the study. Model samples of this alloy containing the Mössbauer isotopes ^{57}Fe and ^{119}Sn were produced. The structure of the model alloy and the technique of its preparation were close to those of industrial alloys. The samples were melted using the method of electric-arc melting with nonexpendable electrode in purified argon atmosphere. Annealing of cold rolled samples and quenching of samples were performed as well as a heat treatment. Cold rolling was carried out in several stages to obtain samples with required sizes, textures and structures. At each stage of the cold rolling followed intermediate annealing at a temperature of 600 ± 5 °C for two hours. Modes of intermediate annealing and final annealing were chosen so that the material was completely recrystallized, and at the same time, there were no β -Nb precipitates. Quenching of samples was carried out in gallium in order to reduce the possibility of the sample saturation with oxygen and hydrogen, which inevitably occurs when quenching in water. Before being placed in the reactor all samples have been deposited in an autoclave for the creation of a protective oxide film.

The irradiation of the samples was carried out in the reactor BOR-60 with fast ($E > 1$ MeV) neutrons both with $2.2 \cdot 10^{25} \text{ m}^{-2}$ and with $11 \cdot 10^{25} \text{ m}^{-2}$ fluences in the temperature region 310–330 °C. The samples were subjected to structural investigations after the irradiation. The irradiated and non-irradiated samples in addition were prepared for the study by Mössbauer spectroscopy. The irradiated samples were thinned to a thickness of 50–80 micron by mechanical polishing. Non-irradiated samples were rolled in foils with a thickness of 40–150 microns. Additional cold rolling was carried out in several stages with intermediate annealing at the selected temperature.

The ^{57}Fe Mössbauer spectra were obtained using spectrometers operating in constant velocity mode with laser stabilization and scintillator detectors, as these spectrometers most accurately provide speed stability. Spectra were obtained at three temperatures: liquid nitrogen (78 K), room (300 K) and intermediate (170 K). A number of programs (UNIVEM MS, DISCOVER, MSTOOLS) were used for spectra fitting. Isomer shifts are given relatively to α -Fe. ^{57}Co in rhodium matrix with an activity of 45 mCi was used as a Mössbauer source.

3 Results

The ^{57}Fe Mössbauer spectra of cold rolled and annealed samples before irradiation (Fig. 1a, b) were fitted by a model, including three doublets [3] corresponding to precipitates of Zr_3Fe with large values of isomeric shift ($\delta \sim -0.4$ mm/s) and quadruple splitting ($\Delta E \sim 1.02$ mm/s), of $\text{Zr}(\text{Nb},\text{Fe})_2$ ($\delta \sim -0.17$ mm/s, $\Delta E \sim 0.20$ mm/s) and of $(\text{Zr},\text{Nb})_2\text{Fe}$ ($\delta \sim -0.15$ mm/s, $\Delta E \sim 0.36$ mm/s). To describe the spectrum of the quenched sample (Fig. 1c) before irradiation a model was chosen based on the lowest possible number of phases and the results of previous work [4]. Spectral components corresponding to precipitates Zr_3Fe , $\text{Zr}(\text{Nb},\text{Fe})_2$, $(\text{Zr},\text{Nb})_2\text{Fe}$, Zr_2Fe ($\delta \sim -0.30$ mm/s, $\Delta E \sim 0.61$ mm/s) and a solid solution of Fe in α -Zr ($\delta \sim -0.07$ mm/s, $\Delta E \sim 0.20$ mm/s) were detected.

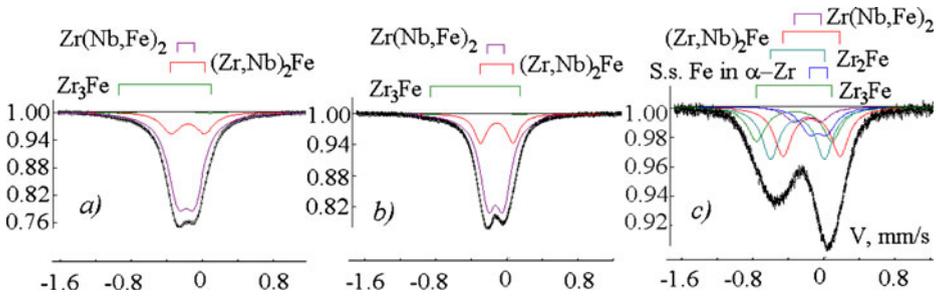


Fig. 1 The ^{57}Fe spectra of E635-type alloy before irradiation: **a** after annealing; **b** after cold rolling; **c** after quenching

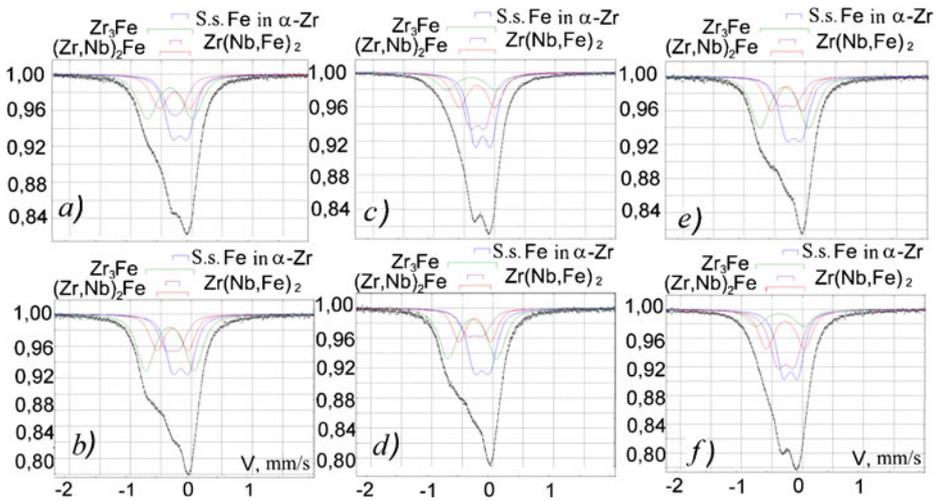


Fig. 2 The ^{57}Fe spectra of E635 alloy (obtained at 300 K): **a** annealed sample irradiated to fluence $2.2 \cdot 10^{25} \text{ m}^{-2}$; **b** annealed sample irradiated to fluence $11 \cdot 10^{25} \text{ m}^{-2}$; **c** cold rolled sample irradiated to fluence $2.2 \cdot 10^{25} \text{ m}^{-2}$; **d** cold rolled sample irradiated to fluence $11 \cdot 10^{25} \text{ m}^{-2}$; **e** quenched sample irradiated to fluence $2.2 \cdot 10^{25} \text{ m}^{-2}$; **f** quenched sample irradiated to fluence $11 \cdot 10^{25} \text{ m}^{-2}$

The irradiation leads to a broadening of the spectra of the rolled and annealed samples (Fig. 2a–d). Such broad spectral lines are typical for the quenched samples (Fig. 1c), where there is a variety of non-equivalent states of iron atoms formed at the expense of the formation of new phases, where there are changes of the nearest environment of the iron atoms in the existing phases and precipitates and where is the presence of a large number of defects. The spectra of samples after irradiation with a fluence of $11 \cdot 10^{25} \text{ m}^{-2}$ (Fig. 2b, d) are very slightly different from those irradiated with a fluence of $2.2 \cdot 10^{25} \text{ m}^{-2}$ (Fig. 2a, c): they are wider and have a more pronounced and intensive left peak. The largest difference is noticed in the spectra of the rolled sample (Fig. 2c, d). The spectrum of the quenched sample after irradiation is also quite strongly changed (Fig. 2e, f). The fitting of spectra was carried out taking into consideration the information about the structure of the alloy, results of TEM investigations of the alloy phase structure (Table 1) [5], results of research on

Table 1 Iron precipitates found by the TEM method in cold-rolled and in annealed E635-type alloy

Before irradiation		After irradiation	
Phase	Structure/lattice	Phase	Lattice
Zr(Nb,Fe) ₂	MgZn ₂ /hcp	–	–
(Zr,Nb) ₂ Fe	Ti ₂ Ni/fcc	(Zr,Nb) ₂ Fe	fcc

Table 2 The relative concentrations of the iron phases found in the E635-type alloy

Treatment	Phase	Irradiated to fluence* 10 ²⁵ m ⁻²		
		No	2.2	11
Annealing	S.s. Fe in α -Zr	–	32 \pm 2	29 \pm 2
	Zr ₃ Fe	1.3 \pm 1.0	35 \pm 3	37 \pm 2
	Zr(Nb,Fe) ₂	75.7 \pm 2.0	16 \pm 2	17 \pm 2
	(Zr,Nb) ₂ Fe	23 \pm 2	17 \pm 4	17 \pm 2
Cold rolling	S.s. Fe in α -Zr	–	34 \pm 2	30 \pm 2
	Zr ₃ Fe	1.9 \pm 1.5	11 \pm 2	38 \pm 3
	Zr(Nb,Fe) ₂	81 \pm 2	33 \pm 3	16 \pm 2
	(Zr,Nb) ₂ Fe	17.1 \pm 3	22 \pm 2	16 \pm 3
Quenching	S.s. Fe in α -Zr	13 \pm 2	30 \pm 2	34 \pm 5
	Zr ₃ Fe	21 \pm 2	38 \pm 4	15 \pm 4
	Zr ₂ Fe	30 \pm 2	–	–
	Zr(Nb,Fe) ₂	8 \pm 2	16 \pm 2	30 \pm 2
	(Zr,Nb) ₂ Fe	28 \pm 2	16 \pm 2	21 \pm 5

non-irradiated samples and assuming the formation of a lot of nonequivalent atom configurations.

The analysis of the Mössbauer spectra of E635-type zirconium alloys irradiated by fast neutrons showed that the iron atoms after both stages of radiation in all samples are in the solid solution in α -Zr and in precipitates Zr₃Fe, Zr(Nb,Fe)₂ and (Zr,Nb)₂Fe. Components are present in the spectra, corresponding to intermetallic precipitates, which are not detected by TEM. This can be explained by the fact that, according to the data of other researchers [1], under irradiation very small precipitates appear in the alloy E635 which are difficult to detect on top of a background of high concentrations of radiation defects and difficult to distinguish from dislocation loops and clusters.

Quantitative analysis of the spectra (Table 2) has shown that under the influence of a neutron irradiation in the E635-type alloy there is a redistribution of iron atoms between phases, depending on initial thermomechanical treatment of an alloy.

The formation of solid solution of Fe in α -Zr occurs and the content of Zr₃Fe increases while the quantity of Zr(Nb,Fe)₂ and (Zr,Nb)₂Fe phases decrease in the annealed sample after the first stage of an irradiation (with a fluence of 2.2·10²⁵ m⁻²). The phase composition of the annealed samples changes slightly upon further irradiation (up to a fluence of 11·10²⁵ m⁻²). In the case of the cold rolled samples irradiated with a fluence of 2.2·10²⁵ m⁻² a considerable increase was observed in the occurrence of the Zr₃Fe phase and in the solid solution of Fe in α -Zr at the expense of the decomposition of the Zr(Nb,Fe)₂ phase as the effect of the neutron irradiation. A further decomposition of the Zr(Nb,Fe)₂ phase occurs together with an increase of the content of the Zr₃Fe phase due to the irradiation with the maximum fluence (11·10²⁵ m⁻²) in the cold rolled samples. The phase composition of annealed and

cold rolled samples are identical after irradiation with the maximum fluence. In the case of quenched samples the amount of solid solution of Fe in α -Zr and the amount of Zr_3Fe and $(Zr,Nb)_2Fe$ phases increase while the quantity of $(Zr,Nb)_2Fe$ phase decreases and a total decomposition of Zr_2Fe phase occurs as the result of irradiation with a fluence of $2.2 \cdot 10^{25} \text{ m}^{-2}$. At the irradiation with the maximum fluence, however, a partial decomposition of Zr_3Fe phase together with the formation of $(Zr,Nb)_2Fe$ phase was observed.

4 Conclusion

^{57}Fe Mössbauer spectroscopy provided qualitative and quantitative data about the phase transformation occurring in zirconium alloy E635 due to irradiation with fast neutrons. The most striking effect was found in the transformation of $Zr(Nb,Fe)_2$ intermetallic compound, which content decreased from $\sim 80\%$ to 16% upon irradiation with a fluence of $11 \cdot 10^{25} \text{ m}^{-2}$. Iron atoms, originating from the decomposition of intermetallic compounds, are incorporated in the solid solution phase of α -Zr and contribute to the formation of Zr_3Fe phase.

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