

# The influence of reactor irradiation on the oxidation state of tin in Zr-0.76Fe-1.6Sn

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Abstract The oxidation states of minor alloying elements in Zircaloys often determine their resistance to corrosion, especially in nuclear reactors. In particular, tin is of interest because of its near ubiquitous use in earlier Zircaloys. To study changes in the oxidation state of tin under irradiation, specimens of Zr-0.76Fe-1.6Sn were corroded at similar conditions in an autoclave and in a nuclear reactor. Corrosion rates were found to be significantly accelerated following irradiation compared to those in the autoclave. Mössbauer spectroscopy revealed that in both the autoclave conditions and reactor conditions, a combination of tetravalent, divalent, and elemental ( $\beta$ -Sn) tin particles are formed during the initial corrosion processes. The kinetics of both the change in tin oxidation state and the corrosion rate in-reactor are greatly accelerated, pointing to the effect of irradiation driving tin into solution more quickly.

Keywords Zirconium alloys · Reactor irradiation · Tin oxidation state · Mössbauer effect

# 1 Introduction and background

In order to develop new alloys with better corrosion resistance for nuclear applications, it is necessary to understand the processes taking place during corrosion both in the metal

This article is part of the Topical Collection on *Proceedings of the International Conference on the Applications of the Mössbauer Effect (ICAME 2017), Saint-Petersburg, Russia, 3-8 September 2017* Edited by Valentin Semenov

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matrix and in oxide films obtained in autoclaves and in reactor conditions. In particular, the oxidation states of minor alloying elements, such as tin and iron, can strongly determine the corrosion behavior of Zircaloys with and without irradiation. Such data can be obtained using nuclear-physical methods such as Mössbauer spectroscopy [1, 2], which can determine the state of tin atoms in zirconium alloys and oxide films.

Many factors help to determine the corrosion resistance of Zircaloys, including strain state in the oxide [3], stabilization of tetragonal or monoclinic phases [4], the presence of grain boundaries [5], oxide "texture" consisting of equiaxed or columnar grains [6], the presence of secondary particle precipitates (SPPs) and their dissolution [7], development of porosity [8] (during "transition" kinetics where the oxide reaches  $2-3\mu$ m in thickness), uptake of hydrogen generated during corrosion [9], and minor alloying elements [10]. This last factor in particular is believed to be due to the partial negation of space charge [11] by doping the oxide with cations of different valence [12], both changing the oxide stoichiometry [13] and alleviating the competition between electronic and ionic conductivity [14], which is believed to strongly limit Zircaloy corrosion in many cases [15]. In particular, the elements tin [16] and iron [17] have been strongly implicated in accelerating corrosion kinetics under irradiation from cubic to more parabolic rate laws under irradiation and following pre-irradiation [18]. It is believed that irradiation ballistically breaks up SPPs [19], causing more tin or iron cations to be driven into solution as oxide dopants. Once there, they can take on valence states lower than +4, locally creating oxygen sub-stoichiometry to preserve charge neutrality [20]. This sub-stoichiometry would then result in more vacant sites for oxygen diffusion [21], accelerating ionic transport, and increase the electronic conductivity of p-doped  $ZrO_2$ , removing the elevtronic limitation [15]. Therefore, it is important to know the precise link between the concentration of dopants like tin in a Zircaloy's oxide under irradiation, though very few techniques can measure these dopants at such low levels, in such small volumes of material. Fortunately, Mössbauer spectroscopy is well-suited to this type of study.

This paper reveals the changes of tin atom oxidation states in oxide films of the zirconium alloy Zr-0.76Fe-1.6Sn during corrosion tests, specifically separating out the effects of simultaneous neutron irradiation. The oxide films are obtained under both autoclave corrosion and neutron irradiation in reactor conditions. Mössbauer spectroscopy is used to show an acceleration in tin oxidation state changes, which correlates well with accelerated oxide kinetics in reactor.

## 2 Experimental

Specimens of the zirconium alloy Zr-0.76Fe-1.6Sn (wt. %) were prepared by electric arc melting, and were sectioned into test coupons  $1 \times 10 \times 15 \pm 0.5$  mm in size. Detailed methods of alloy and specimen preparation are described in [12]. Oxide films were grown during both autoclave corrosion and similar conditions with simultaneous neutron irradiation. Before corrosion all samples were annealed at 580 °C for 3 hours to normalize the grain structures. Corrosion testes were carried out in a laboratory autoclave and in reactor conditions, both at 350 °C and a pressure of 16.8 MPa. The total neutron fluence applied was  $3*10^{20}$  n/cm<sup>2</sup> (E>0.5 MeV), and specimens were irradiated in the RBT-10 reactor in Dimitrovgrad, Russia. Specimens were exposed to their respective environments for up to 120 days in an autoclave, or up to 112 days of exposure in the RBT-10 reactor.

All oxide films grown on test specimens were investigated by the Mössbauer spectroscopy method, while coupon weight gains were measured on a balance with 0.05 mg



Fig. 1 Kinetic curves of corrosion for Zr-0.76Fe-1.6Sn exposed at 350 °C and 16.8 MPa in autoclave and reactor conditions, showing significantly more rapid corrosion in reactor conditions

sensitivity. Weight gain  $(\Delta m)$  was converted to oxide thickness (d) using the following equation:

$$d = \frac{123 \ \Delta m}{32 \ \rho_{ZrO_2}}$$

Where  $\rho_{ZrO_2}$  is the density of ZrO<sub>2</sub>, taken at 5.68 g/cm<sup>3</sup>, and 123 & 32 are the molar masses of ZrO<sub>2</sub> and O<sub>2</sub>, respectively. It is assumed that all O<sub>2</sub> absorbed forms ZrO<sub>2</sub>, and that all the measured weight gain is due to ZrO<sub>2</sub> formation. For Mössbauer investigations the ZrO<sub>2</sub> oxide was separated from the metallic part of alloy by dissolving the metal part in a 0.3% water solution of HF. Mössbauer experiments were conducted at room temperature, using a spectrometer operating in constant acceleration mode. Isomer shifts are given relative to the calibration compound BaSnO<sub>3</sub>.

#### 2.1 Corrosion experiments

Kinetic curves of alloy corrosion, both for in-autoclave and in-reactor specimens, are given in Fig. 1. In laboratory autoclave experiments, lustrous, black oxide films were observed on the surfaces of all alloy samples. This observation remained unchanged from the beginning to the end of corrosion tests. The film thicknesses increased from nearly zero to  $1.4\mu$ m during the corrosion tests.

During the same period of corrosion occurring in irradiation conditions, more matte, dark grey oxide films formed on the samples of alloys, with a maximum thickness of  $4.7\mu$ m. It is known that the color of the oxide film partially indicates its protective properties, and characterizes expected corrosion properties of alloys. The dark grey color indicates a lower corrosion resistance in reactor conditions. The reactor tests lead to a significant increase of the film thickness by approximately three times (see Table 1).

Corrosion time, days	h, $\mu$ m	SnO <sub>2</sub>	SnO	Sn <sup>+4</sup> in ZrO <sub>2</sub>	$\beta$ -Sn	with O <sub>2</sub>	without O <sub>2</sub>
Corrosion in a	autoclave	at 350 °C and	1 16.8 MPa				
40	0.8	$0.20{\pm}0.05$	$0.45{\pm}0.09$	$0.14{\pm}0.04$	$6.5 {\pm} 2.0$	$7.3 {\pm} 2.2$	$9.8 {\pm} 2.9$
80	1.3	$0.96{\pm}0.29$	$0.58{\pm}0.20$	$0.33 {\pm} 0.10$	$18.0 {\pm} 5.4$	20±6	$26.8{\pm}7.8$
120	1.4	$0.71 {\pm} 0.20$	$1.2{\pm}0.4$	$0.13 {\pm} 0.04$	$4.4{\pm}1.4$	$6.5 {\pm} 2.1$	$8.8{\pm}2.8$
Corrosion in reactor at 350 °C and 16.8 MPa							
37	3.8	$0.22{\pm}0.06$	$0.31 {\pm} 0.08$	$\sim 0.04$	-	$0.6 {\pm} 0.2$	$0.8 {\pm} 0.2$
80	4.5	$0.13 {\pm} 0.04$	$0.17 {\pm} 0.05$	$\sim 0.04$	$0.13 {\pm} 0.04$	$0.47{\pm}0.14$	$0.6{\pm}0.2$
112	4.7	$0.13{\pm}0.04$	$0.20{\pm}0.06$	$\sim 0.05$	$0.09{\pm}0.03$	$0.49{\pm}0.20$	$0.66{\pm}0.27$

Table 1 Concentration of Sn (wt. %) in oxide films as measured by Mössbauer spectroscopy

#### 2.2 Mössbauer investigations

Mössbauer spectra of <sup>119</sup>Sn in oxide films grown on Zr-0.76Fe-1.6Sn are shown in Figs. 2 and 3. The spectra are obtained at room temperature. One can see in this figure that the shapes of the spectra vary during the corrosion tests, which indicates a change in the oxidation states of tin atoms in the separated oxide films. In these spectra, lines of hyperfine magnetic splitting are not observed, indicating the absence of tin magnetic phases in the oxide films. The spectra consist of single lines and lines of hyperfine quadrupole splitting of paramagnetic phases. On the left side of all spectra there are lines of hyperfine quadrupole splitting with an isomer shift (IS) of IS= $0.00\pm0.05$  mm/s and quadrupole splitting (QS) of QS= $0.35\pm0.05$  mm/s.

These Mössbauer spectra parameters coincide with parameters of tin in SnO<sub>2</sub>. Next, a line with IS=0.74±0.05 mm/s was identified as the line of Sn<sup>4+</sup> ions in solid solution in ZrO<sub>2</sub>. Lines of hyperfine quadrupole splitting of the third paramagnetic phase with IS=2.8±0.1 mm/s and QS=1.7±0.1 mm/s were identified as the lines of SnO with a tetragonal modification [2, 22]. Another line of a paramagnetic phase with IS=2.65±0.06 mm/s was found in the spectra (most instances of this line are in the spectra obtained in autoclave experiments). It is known that such isomer shifts are typical of metallic  $\beta$ -Sn.

The previous results of Mössbauer studies [2, 23–25] at liquid nitrogen temperature (77 K) showed that the intensity of the identified line increased. Large variations of the resonance absorption, and as a consequence a large increase in line intensity, are characteristic of  $\beta$ -Sn [2, 23–26]. The variation of the resonance absorption probability in the 78–300 K temperature interval for this phase turned out to be close in magnitude to the variations of f' that were also observed for metallic tin ( $\beta$ -Sn). Concentrations of tin atoms in different chemical states were determined in all oxide films, with results shown in Table 1.

Analysis of the data in Table 1 shows that  $\beta$ -tin precipitates were formed in the all oxide films obtained in both autoclave and reactor conditions. Large quantities of  $\beta$ -Sn are formed in ZrO<sub>2</sub> obtained in autoclave, while concentrations of SnO<sub>2</sub> and SnO in oxide films obtained in autoclave and reactor conditions differ significantly. Reactor irradiation decreases the concentration of  $\beta$ -Sn in oxide films, favoring tin-oxygen compounds instead. This is strong evidence of increased tin doping of ZrO<sub>2</sub> in reactor irradiation conditions.



**Fig. 2** Mössbauer spectra of <sup>119</sup>Sn in oxide films obtained during corrosion in autoclave: **a** 40 days, **b** 80 days, **c** 120 days. Black curves are the original data, while the smooth blue and green curves represent model fits to the spectra

## **3** Discussion

It is most useful to link phase fractions containing tin directly to observed oxidation rates in the two different conditions. The comparative analysis of the corrosion kinetic curves shows that corrosion is slower in an autoclave than in reactor irradiation conditions, as was also shown in a recent study [27]. In this paper, increased susceptibility to corrosion was explained by simultaneous radiation-induced defect formation and dissolution of intermetallic precipitates, known as secondary particle precipitates (SPPs), which impart much of the corrosion resistance in many Zircaloys. The authors of this paper could not confirm the existence of  $\beta$ -Sn, SnO, or SnO<sub>2</sub> in their oxide films, as the SPPs present may have been in the amorphous state due to radiation-induced amorphization. In our investigations we revealed that oxides obtained in reactor conditions contain small quantities of  $\beta$ -Sn. These precipitates, as the authors of references [2, 22, 25, 26] assume, have a positive, slowing effect on



Fig. 3 Mössbauer spectra of  $^{119}$ Sn in oxide films obtained during corrosion in reactor: **a** 37 days, **b** 112 days. The lower, purple plots represent the error between the observed and modeled Mössbauer spectra

the corrosion process. In the oxide films obtained in reactor irradiation conditions, most tin is found as  $SnO_2$  and SnO, correlating directly to the accelerated oxidation kinetics compared to autoclave exposures. This strongly suggests that the observed doping of  $ZrO_2$  by Sn is at least partially responsible for the accelerated corrosion kinetics, whether directly by changing stoichiometry and electronic/ionic conductivities or by changing the texture of the grown oxide film.

## 4 Conclusion

This research has shown that corrosion of Zr-0.76Fe-1.6Sn proceeds more quickly in reactor conditions than in autoclave conditions, which itself is likely caused by irradiation-induced tin doping of the oxide film. It has been determined that tin atoms in oxide films are in the states of SnO, SnO<sub>2</sub>, in the form of solid solutions of Sn<sup>4+</sup> ions in ZrO<sub>2</sub>, and  $\beta$ -Sn.

Tin atoms are redistributed in films during corrosion, particularly while under simultaneous irradiation. The data obtained confirm the idea of the positive effect of metal precipitates in oxide films on corrosion resistivity of zirconium alloys during corrosion, by binding up minor alloying elements and preventing oxide doping from inducing sub-stoichiometry. Future work will determine similar results for the state of iron in this alloy, as well as guiding studies of new Zircaloys which can keep minor alloying elements bound in less corrosion-inducing oxidation states. In particular, the ability to retain SPPs or other bound forms of minor alloying elements would represent a boost to the resistance of Zircaloys to simultaneous corrosion and irradiation found in light water reactors.

**Acknowledgements** The work was financially supported by MEPhI's Competitiveness Program. A. F. Dykhuis and M. P. Short acknowledge funding from the Consortium for the Advanced Simulation of Light Water Reactors (CASL), a U.S. Department of Energy (DOE) Energy Innovation Hub.

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