CrossMark

Mössbauer study of oxide films of Fe-, Sn-, Cr- doped zirconium alloys during corrosion in autoclave

V. P. Filippov[1] · A. B. Bateev[1] · Yu. A. Lauer[1]

Abstract Mössbauer investigations were used to compare iron atom states in oxide films of binary Zr-Fe, ternary Zr-Fe-Cu and quaternary Zr-Fe-Cr-Sn alloys. Oxide films are received in an autoclave at a temperature of 350–360 °C and at pressure of 16.8 MPa. The corrosion process decomposes the intermetallic precipitates in alloys and forms metallic iron with inclusions of chromium atoms α–Fe(Cr), α–Fe(Cu), α–Fe$_2$O$_3$ and Fe$_3$O$_4$ compounds. Some iron ions are formed in divalent and in trivalent paramagnetic states. The additional doping influences on corrosion kinetics and concentration of iron compounds and phases formed in oxide films. It was shown the correlation between concentration of iron in different chemical states and corrosion resistance of alloys.

Keywords Zirconium alloys · Oxide film · Corrosion · Mössbauer effect

1 Introduction

Zirconium alloys are used as materials for claddings of nuclear reactors. The extension of operating time of fuel rods up to 6-7 years and increasing the burning out of fuel to 60–70 MW days/kgU depend on corrosion resistance of zirconium alloys. To create new corrosion-resistant alloys, it is necessary to understand the processes in the oxide films during corrosion of zirconium alloys especially in a steam environment similar to reactor conditions. Such knowledge are needed for understanding the influence of additional

✉ V. P. Filippov
vpfilippov@mephi.ru

[1] National Research Nuclear University "MEPhI" (Moscow Engineering Physics Institute), Kashirskoe shosse, 31, Moscow 115409, Russia

 Springer

doping by different elements. The most used alloying elements are tin, copper, chromium, iron, tungsten and nickel. Iron has Mössbauer isotope [57]Fe and so the Mössbauer spectroscopy can be used to determine the oxidation state of Fe in ZrO_2 matrix. Zirconium alloys and their oxide films have been widely studied [1–7]. The influence of chromium and tin on iron states in zirconium alloys and their oxide films is described in [1, 2]. Bozzano [2] determined iron state in Cr-doped zirconium alloys and showed the presence of $\alpha-$Fe and iron oxides in ZrO_2. In papers [5–7] the zirconium oxidizes prepared by calcination were studied. The existence of iron paramagnetic and magnetic phases has been shown in these oxides. In [1, 3, 4] some zirconium oxides have been obtained in autoclave. These oxides were found to be complex composition too. But there was no comparison iron atoms distribution in oxides of different alloys especially with oxides of Cu-doped Zr-alloys.

The aim of this paper is to obtain a data about iron atomic states and its redistribution in oxide films obtained during corrosion in autoclave at temperature of (350-360) °C for binary Zr-Fe, ternary Zr-Fe-Cu and quaternary Zr-Fe-Cr-Sn alloys.

## 2 Sample preparation and experimental methods

Three zirconium based alloys (binary Zr-1.24 wt%Fe, ternary Zr-1.39 wt %Fe-0.60 wt %Cu and quaternary Zr-1.0wt%Fe-0.50wt%Cr-1.2wt%Sn) were prepared. The iron concentration differs slightly, so any differences in the corrosion behavior and in the iron atoms redistribution can be caused by the presence of other elements in the alloy. The alloy specimens were melted in an electric arc furnace using W electrode in clean argon atmosphere. The melting was carried out more than five times. Then the samples of alloys were subjected to thermo-mechanical treatment with the technology described in [1, 3, 4]. The samples were rolled approximately to thickness of 800 microns, and were annealed at 650 °C for 2 hours. These samples were exposed to corrosion tests that were carried out in stainless steel autoclaves at temperature of (350-360) °C and pressure of 16.8 MPa. The oxide films were separated by dissolving of the metal substrate in the 3 % solution of fluoric acid [1, 3]. The absorbers for Mössbauer measurements are prepared from the oxide films thus obtained [1, 3]. [57]Co in Cr matrix has been used as Mössbauer source. The spectra were obtained using Mössbauer spectrometer operating at constant acceleration mode at room temperature. The spectra were fitted using the Mössbauer program UNIVEM MS. The technique described in [8] was used to determine the absolute concentrations of iron atoms.

3 Results and discussion

3.1 Kinetics of corrosion

The kinetic curves of corrosion tests are presented in Fig. 1. The oxide films on alloys had a black color and were strongly adhered to the metal in initial stages of corrosion.

For Zr-Fe alloy some whitened points were detected under microscopic examination on the surface of the oxide film with the thickness of 2.8 microns. The quantity of points
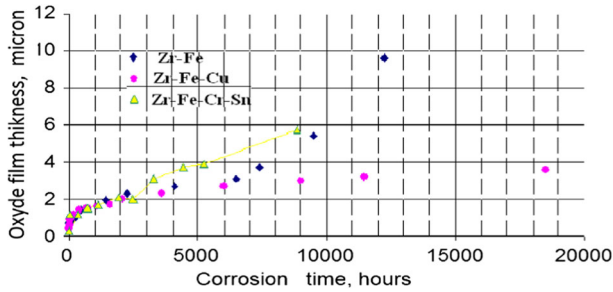
Fig. 1 Kinetic curves of zirconium alloys during corrosion in autoclave at t=350 ° C, p=16.8 MPa

increases with increasing film thickness. The analysis of kinetic curves in Fig. 1 shows that in initial stages of corrosion the growth of oxide film thickness of all alloys is almost similar, with approximately equal exponents.

The thicknesses of oxide film of binary alloy are a little greater than those of ternary alloy with copper. Approximately at 6500 hours, we observed the transition to linear (brake-away corrosion on kinetic curve of the binary alloy

Transition to brake-away corrosion for the quaternary alloy comes earlier than that of other alloys, but the rate of oxide film thickness increase is less than that for the binary alloy. The specimens of ternary alloy have the lowest rate of oxide film growth. Corrosion properties of the quaternary alloy can be explained by the presence of tin atoms in alloy [3]. In [3] it was shown, that in ternary alloy Zr-1.4 wt%Fe - 0.7 wt%Cr after 4650 hours of corrosion the thickness of oxide film was 2.2 mm, under similar conditions of corrosion. It is evident that at long-term corrosion test the oxide film thickness is less for this alloy than for quaternary one. The thickness of oxide film of ternary alloy increases according to parabolic law until the end of corrosion tests (about 18000 h). This means that the ternary alloy Zr-Fe-Cu has higher corrosion resistance than binary alloy Zr-Fe. Taking into account that preparation processes of alloys and corrosion tests of specimens were identical, the differences are only due to presence of copper atoms in the ternary alloy. Hence it can be assumed that copper influences positively on the corrosion resistance of ternary alloy.

3.2 Mössbauer data

Mössbauer spectra of some oxide films are presented in Fig. 2 and Fig. 3. The spectra have superposition of the lines of magnetic phases and lines of paramagnetic phases.

In binary and ternary alloys iron environment is similar to intermetallic compound Zr_3Fe with quadrupole splitting Mössbauer spectra (QS=0.75-0.85 mm/s). In the quaternary alloy iron environment is similar to intermetallic compound $Zr(Fe,Cr)_2$ [2, 3] with QS=(0.18-0.25) mm/s. The shape of Mössbauer spectra changes during different stages of alloy corrosion, conclusively showing the redistribution of iron atoms in oxide films. All spectral lines are broadened. The broadening of the lines can be caused by the superposition of lines of different phases with similar parameters of the spectra, associated with non-stoichiometry
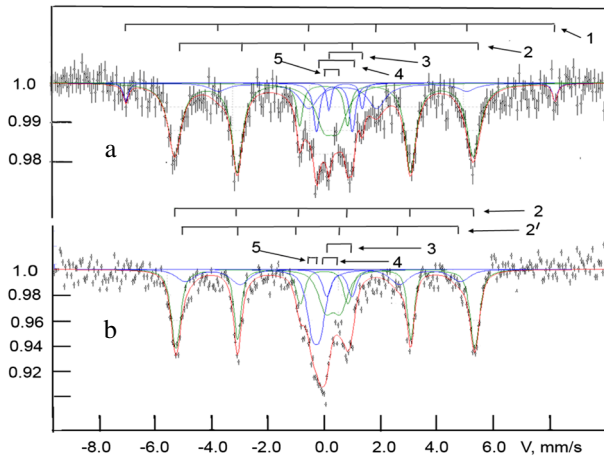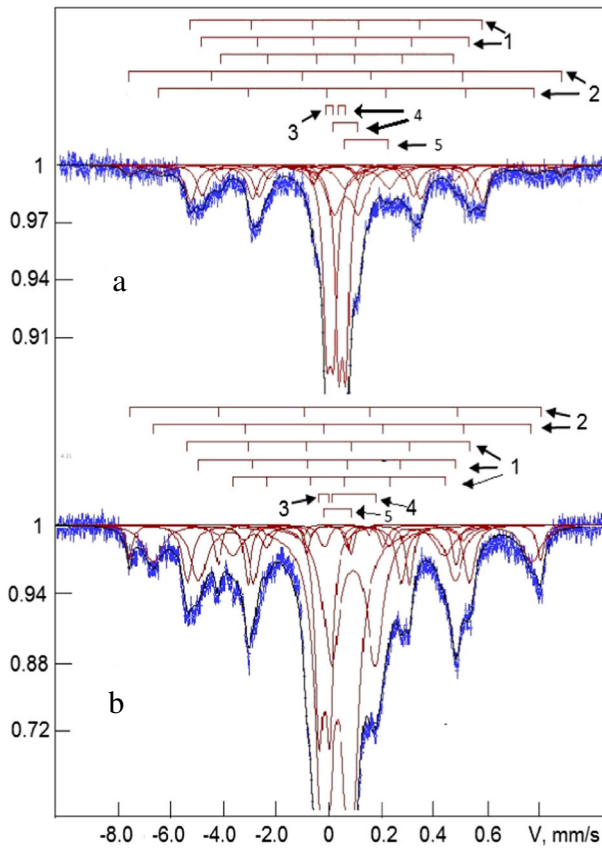
Fig. 2 Transmission Mössbauer spectra of ^{57}Fe in oxide film **a**) 2,2 μm thickness after 1136 hours of corrosion of Zr-1.24%Fe alloy, **b**) 3.2 μm thickness after 8100 hours of corrosion of Zr-1.39 wt %Fe-0.60 wt %Cu alloy. 1) $\alpha-Fe_2O_3$, 2, 2') solid solution (ss) Cu in $\alpha-Fe$, 3) ss Fe^{2+} in ZrO_2, 4) ss Fe^{3+} in ZrO_2, 5) unknown

of compounds and with defects in their crystal lattice. The analysis of spectra (Fig. 2) has shown, that in oxide films there are such iron compounds: 1) $\alpha-Fe_2O_3$, 2) and 2') solid solution (ss) Cu in $\alpha-Fe$, 3) ss. Fe^{2+} in ZrO_2, 4) ss. Fe^{3+} in ZrO_2, 5) unidentified phase. Concentration of iron atoms in phases and precipitates are calculated and the data are shown in Tables 1 and 2. The isomer shift of the unidentified phase is changed in the range of (-0.15 – 0) mm/s. The state of iron, giving such line in the spectra, is difficult to identify at this stage of investigations.

The analysis of spectra of the quaternary alloy (Fig. 3) has shown that in oxide films of this alloy the iron atoms are in a form of solid solution of chromium atoms in $\alpha-Fe$, a solid solution of divalent and trivalent iron atoms in ZrO_2 and unlike of binary and ternary alloys the lines of compound Fe_3O_4 are clearly shown here. Practically all these iron phases were observed in oxides studied in [2]. The spectral lines of this compound are broadened. It may be caused due to some iron atoms in Fe_3O_4 are displaced by chromium atoms during oxidation of metallic precipitates.

The values of total concentration of iron in thin films are more than 2 times lower, than in the alloys. One of these reasons can be the dissolution of some iron contained particles during separation of oxide films. Another reason may be associated with reducing of resonant absorption probability in small precipitates. For a thick film of the quaternary alloy the value of the total concentration of iron in the oxide film is close to the concentration in the alloy. The analysis of the spectra and the data of table shows, that before transition to the catastrophic corrosion stage the concentration of iron in oxide films in the form of oxide $\alpha-Fe_2O_3$ is very small or absent totally in a ternary alloy. For the binary alloy, the concentration of $\alpha-Fe_2O_3$ in oxide films sharply increases in a region of transition to catastrophic corrosion. For the quaternary alloy, the concentration of compound Fe_3O_4 sharply increases

Fig. 3 Transmission Mössbauer spectra of ^{57}Fe in oxide film of Zr-Fe-Cr-Sn alloy **a**) 1.6 μm thickness after 1128 h of corrosion, **b**) 3.6 μm thickness after 4476 h of corrosion. 1) solid solution (ss) Cr in $\alpha-$Fe, 2) Fe_3O_4, 3) $Zr(Fe,Cr)_2$, 4) ss Fe^{2+} in ZrO_2, 5) ss Fe^{3+} in ZrO_2

in oxide films after transition to linear corrosion law. So for binary and quaternary alloys after transition to catastrophic corrosion the growth of oxide compounds concentration is observed. In oxide films of the ternary alloy such phenomenon is not observed. The absence of brake-way on its kinetic curve of corrosion testify god corrosion resistance of the ternary alloy. The absence of the growth of iron oxide compounds concentration in oxide films of this alloy demonstrates the correlation between quantity of iron oxides and kinetics curve of corrosion.

The relative concentration of iron in the form unidentified paramagnetic phase in oxide films of the ternary alloy is more than in the films of binary alloy. These data allow us to propose that corrosion resistance correlates with concentration of iron atoms remaining in the form of metal iron $\alpha-$ Fe and in unknown paramagnetic phase. Thus, the doping of copper atoms to zirconium alloy increases the relative concentration of $\alpha-$ Fe particles in oxide films and increases the corrosion resistance of alloy.

Table 1 The concentration of iron (mas. %) in specimens of oxide films of the binary and ternary alloys subjected to corrosion tests in the autoclave at T=350 ° C, p=16.8 MPa

Alloy composition	Thickness, μm.	Time of corrosion h	$\alpha-$Fe	$\alpha-$Fe$_2$O$_3$	Solid solution Fe^{3+} in ZrO$_2$	Solid solution Fe^{2+} in ZrO$_2$	Unidentified phase	Total of Fe	Total of Fe without O$_2$
Zr-1.24 %Fe	1.0	263	-	-	~ 0.02	0.40±0.08	0.09±0.03	0.50±0.20	0.67±0.20
	2.0	1424	0.11±0.02	~ 0.02	0.08±0.02	0.13±0.03	0.09±0.03	0.42±0.12	0.57±0.12
	3.0	6906	0.11±0.03	0.19±0.03	0.06±0.02	0.18±0.04	0.05±0.02	0.60±0.20	0.81±0.20
	4.2	8060	0.06±0.02	0.12±0.02	~ 0.02	0.11±0.02	~ 0.02	0.33±0.10	0.44±0.10
	9.6	12235	0.09±0.03	0.30±0.10	-	0.16±0.04	~ 0.02	0.60±0.20	0.81±0.20
	12.0	15554	0.06±0.03	0.30±0.10	~ 0.02	0.12±0.04	~ 0.02	0.50±0.20	0.67±0.20
Zr-1.39 %Fe-0.60%Cu	1.1	200	-	-	-	0.30±0.20	0.13±0.09	0.40±0.30	0.54±0.30
	2.1	2600	~ 0.03	0.06±0.03	-	0.10±0.03	0.04±0.02	0.20±0.10	0.27±0.10
	2.5	4600	0.06±0.03	0.07±0.03	-	0.24±0.04	0.07±0.03	0.40±0.10	0.54±0.10
	3.2	8100	0.10±0.03	-	-	0.07±0.02	0.05±0.02	0.22±0.07	0.30±0.07

Table 2 The concentration of iron (mas. %) in specimens of oxide films of the quaternary alloys subjected to corrosion tests in autoclave at T=360° C, p=16.8 MPa

Alloy composition	Thickness, μm.	Time of corrosion h.	$\alpha-$Fe	Fe$_3$O$_4$	Solid solution Fe^{2+} in ZrO$_2$	Solid solution Fe^{3+} in ZrO$_2$	ZrFeCr	Total Fe	Total Fe without O$_2$
Zr-1.0% Fe-0.5% Cr-1.2%Sn	1.6	1128	0.07±0.02	0.02±0.03	0.02±0.03	0.08±0.03	0.09±0.03	0.3±0.1	0.4±0.2
	3.6	4476	0.15±0.03	0.17±0.03	0.17±0.02	0.11±0.03	0.05±0.03	0.6±0.2	0.8±0.2
							−		

4 Conclusions

The oxide films of binary Zr-1.24 wt%Fe, ternary Zr-1.39 wt %Fe-0.60 wt %Cu and quaternary Zr-1.0wt%Fe-0.50wt%Cr-1.2wt%Sn are received in autoclave conditions at temperature of 350 ° C and pressure of 16.8 MPa and investigated by Mössbauer spectroscopy. It is shown, that doping of copper to binary zirconium alloy increases corrosion resistance of the alloy. In the oxide films the compounds and phases such $\alpha-$ Fe$_2$O$_3$, Fe$_3$O$_4$, solid solution (ss) of Cu and Cr atoms in $\alpha-$ Fe, ss. Fe^{2+} in ZrO$_2$, ss. Fe^{3+} in ZrO$_2$, unknown phase were found.

The better corrosion resistance of ternary alloy accompanied with relative high concentration of metal precipitates of $\alpha-$ Fe in oxide film. The existence of great concentrations of $\alpha-$ Fe and low concentration such compounds as $\alpha-$ Fe$_2$O$_3$, and Fe$_3$O$_4$ during all long-term corrosion tests may be due to the presence of copper atoms in alloy.

References

1. Pecheur, D., Filippov, V.P., Bateev, F.B., Ivanov, Y.Y.: Mössbauer Investigations of the Chemical States of Tin and Iron Atoms in Zirconium Alloy Oxide Film Zirconium in the Nuclear indystry13 international symposium ASTM STR 1423, Cherry D Moan, Eds. ASTM international, PA, pp. 135–153 (2002)
2. Bozzano, P.B., Ramos, C., Saporiti, F., Vazquez, P., Versaci, R., Saragovi, C.: Oxidation of the hexagonal Zr(Cr0,4Fe0,6)2 Laves phase. JNM **328**, 225–231 (2004)
3. Babikova, Y.F., Gruzin, P.L., Filippov, V.P., Ivanov, A.V.: Nuclear gamma resonance researches of correlation between corrosion kinetic and atoms redistribution of doped elements in oxide films of zirconium alloys Ivestia Vuzov, physic part, vol. 1, 70–74 (1981)
4. Filippov, V.P., Bateev, A.B., Lauer, Y.A., Kargin, N.I., Petrov, V.I.: Changes in the state of iron atoms in Zr alloys during corrosion tests in an autoclave. Hyperfine Interact. **226**(1-3), 771-779 (2014)
5. Berry, F.I., Simon, J., Smith, M.R.: Iron-zirconium oxide catalysts for the hydrogenation of carbon monoxide in situ studies by iron 57 Mössbauer spectroscopy. Hyperfine Interact. **46**, 607–611 (1989)
6. Marest, G., Donnet, C., Sawicki, J.A.: Annealing behavior of iron implanted zirconia. Hyperfine Interact **56**, 1605–1612 (1990)
7. Berry, F.J., Skinner, S.J.: ^{57}Fe Mossbauer spectroscopic study of iron-doped zirconium (IV) oxide. Proceedings of the ICAME '97 Conference: In Memoriam of Professor Jacques Danon. In: Baggio Saitovitch, E., Rechenberg, H., Scorzelli, R.B. (eds.)
8. Filippov, V.P., Petrov, V.I., Lauer, D.E., Shikanova, Y.A.: Calculation of absolute concentrations and probability of resonant absorption for iron bearing precipitates in zirconium alloys. Hyperfine Interact. **168**, 965–971 (2006)