Iron atoms redistribution in oxide films of Zr-Fe, Zr-Fe-Cu alloys during corrosion in autoclave at 350°C

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Abstract. The data on changes of iron atoms state in the oxide films of binary Zr-1.24 mas.%Fe and ternary Zr-1.39 mas.%Fe-0.60 mas.%Cu zirconium alloys are obtained. Alloys are subjected to corrosion tests under autoclave conditions at 350°C temperature in a steam-water environment under pressure p = 16.8 MPa. In initial specimens of the alloys the iron atoms are in the form of intermetallic compounds. In oxide films the decomposition of intermetallic compounds and formation of new compounds occurs with structural phase distortion. In the oxide films metallic the metallic iron particles $\alpha-$Fe, iron oxide in the form of hematite $\alpha-Fe_2O_3$, solid solutions of iron ions in ZrO_2 are formed. The phase composition of the oxide films depends on the alloy composition and changes during the growth process of the oxide film.

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 of fuel from 35 to 70 MWt days/kg U [1] depend on corrosion resistance of zirconium alloys. To create the new corrosion-resistant alloys it is necessary the understanding of the processes in the oxide films during corrosion of zirconium alloys especially in a steam environment closed to reactor conditions. The same data are needed for understanding the influence of additional doping of different elements. The perspective alloying elements are tin, copper, chromium, iron, tungsten and nickel. Iron has Mössbauer isotope [57]Fe and therefore Mössbauer spectroscopy can be used to study the redistribution of iron atoms in oxide films. The aim of this paper is to obtain the data about the redistribution of the iron atom states in oxide films during corrosion in autoclave at the temperature of 350 °C, for binary Zr-Fe and ternary Zr-Fe-Cu. alloys.

2. Experimental

Two zirconium based alloys Zr-1.24 mas.%Fe and Zr-1.39 mas.%Fe-0.60 mas.%Cu were prepared. The iron concentration differs slightly, so any differences in the corrosion behaviour and in the iron atoms redistribution can be caused by the presence of copper in the alloy. The alloy specimens were melted in an electric arc furnace using nonconsumable tungsten electrode in an argon atmosphere, and then subjected to thermo-mechanical treatment with the technology described in [1, 2]. Then the samples were rolled approximately to thickness of 800 microns, and were annealed at 650 °C during 2 hours. Corrosion tests were carried out in stainless steel autoclaves at temperature 350 °C, with 16.8
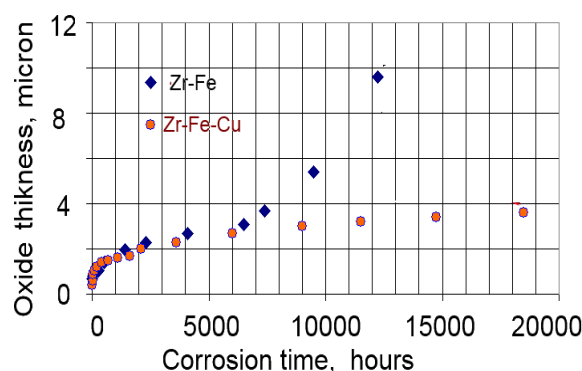
MPa pressure. Oxide films were separated from the metal by dissolving the metal substrate in 3% solution of hydrofluoric acid. From the obtained oxide films the absorbers were prepared for Mössbauer studies [2]. ^{57}Co (Cr) was used as a Mössbauer source. The spectra were obtained using the Mössbauer spectrometer operating at constant acceleration mode at room temperature. The spectra were fitted using Mössbauer programs Univem MS. The technique of determining the absolute concentrations of iron atoms described in [4].

3. Results and discussion
3.1. Kinetic of corrosion
The kinetic curves of corrosion tests are shown in Figure 1. During initial stage of corrosion the oxide films on alloys were strongly adhered to the metal and had a black color. For Zr-Fe alloy some whitened grains were detected under microscopic examination on the surface of the oxide film with thickness of 2.8 microns. The number of grains increases with increasing film thickness. The analyze of kinetic curves shows that in initial stage of corrosion the growth of oxide film thicknesses are almost parallel, with approximately equal exponents. The oxide film thicknesses of binary alloy a little more than those of ternary alloy with a copper. Approximately at 6500h the transition to catastrophic corrosion (breakaway) is detected for binary ally. For the ternary alloy, the oxide film thickness increase according to parabolic law until the end of corrosion tests (about 18000 h). This means that the ternary alloy Zr-Fe-Cu has a higher corrosion resistance than binary alloy Zr-Fe. Taking in to account that all the processes for the preparation of samples and corrosion tests were identical and the only differe nce is the presence of copper in the second alloy, one can assumed that there are the effect of copper in this alloy. The effect of copper on the redistribution of iron atoms in oxide films can be explained from the analysis of Mössbauer spectra of oxide films.
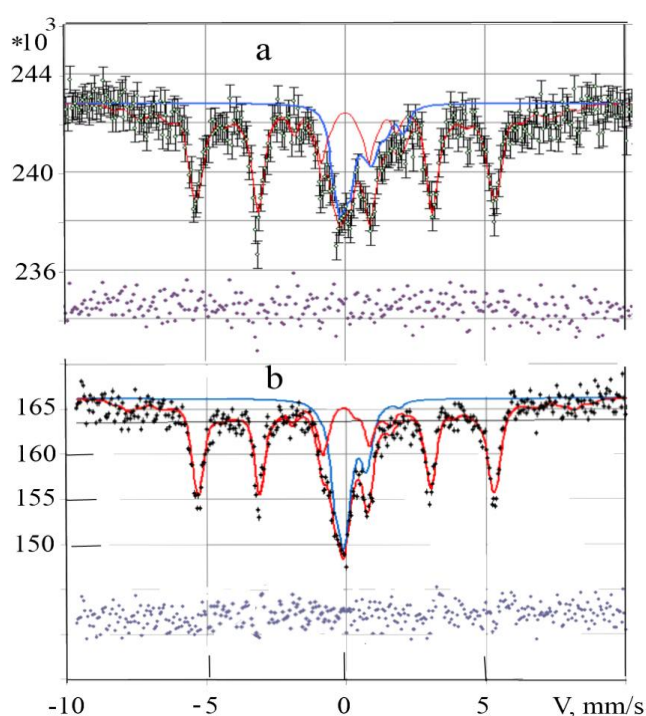

Figure 1. Kinetic corrosion curves of zirconium alloys tested in autoclave at 350 °C temperature, and 16.8 MPa pressure.

3.2 Mossbauer data
Mössbauer spectra of some oxide films are presented in Figure 2. One can see the superposition of the lines of magnetic hyperfine splitting of the magnetic phases and lines of the quadrupole splitting of the paramagnetic phases. Practically 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 of compounds and defects in the crystal lattice. Analysis of the spectra is made using the previously obtained data [1, 2]. These spectra are fitted with programme MSTools [3] giving the distributions of quadrupole splitting and hyperfine magnetic fields (HMF). The obtained distributions are shown in Figure 3. One can see the differences in spectra because Mössbauer spectroscopy is sensitive to the local and crystallographic environment. Each distinct crystallographic, magnetic and chemical environment for Fe forms different Lorentzian lines in the Mössbauer spectrum. That's why in complex absorbers there are the local distortions and atomic
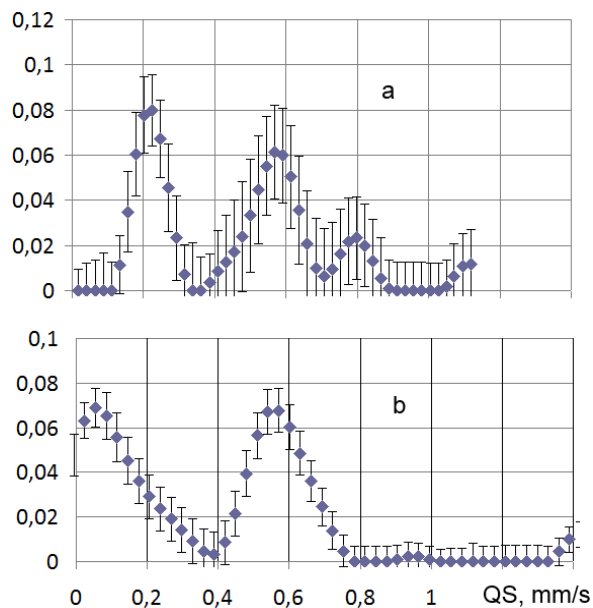
disorder surrounding the Fe atoms, rather than simply reflecting the ideal point symmetries of the relevant sites. The lines of spectra have large width lines because of some distribution of hyperfine magnetic fields and quadrupole splitting. The sextets of the field distribution were constrained to an area 3:2:1 with linewidth of 0.25 mm s^{-1}. The steps of ~0.14 T for the magnetic field distribution were used. The results are shown in Figure 4. The isomer shift was allowed to vary linearly with the magnetic hyperfine field. The magnetic field distribution may reflect a wide distortion in particle size and the presence different form of iron oxides. Intensive pick is in the region of 33.0 T for both spectra (Figure 4) of samples. These picks associate with presence of particles of α–iron in oxide films. The presence of picks with low intensities in the region of ~30 and ~27 T (Figure 4 b) can be explained by influence of Cu atoms in alloy. Such magnitudes of hyperfine magnetic fields can reflect the presence of sold solutions of Cu atoms in the iron particles. Such picks are not observed for sample of binary alloy. For both oxide samples the picks of HMF of ~18.0 T are observed with relative intensities of ~ 0.04.
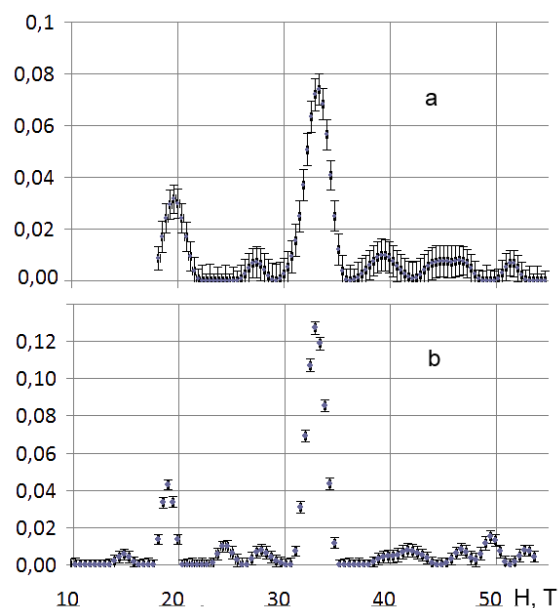

Figure 2. Transmission Mössbauer spectra of ^{57}Fe in: a) oxide film of 2.2 μm on alloy (Zr-1,24 mas.% Fe) after 1136 h of corrosion, b) oxide film of 3.2 μm on alloy (Zr-1,39 mas.% Fe-0.60 mas.% Cu) after 8100 hours of corrosion.

These picks may deal with the presence of intermetallic compound $ZrFe_2$. $ZrFe_2$ can be formed in the process of oxidation of intermetallic compound Zr_3Fe. As Zr is more active in interaction with oxygen the Zr atoms leave intermetallic compound Zr_3Fe and formed crystals of ZrO_2. In the Zr_3Fe particles the deficit of Zr atoms can takes place. This situation promotes to formation of particles $ZrFe_2$. In further process of corrosion these particles are oxidized too. That's why the lines of $ZrFe_2$ particles were not observed in conversion electron Mössbauer spectroscopy (CEMS) spectra. CEMS spectra reflect information from surface layers in which full oxidation is realized. As to pick with magnitude of magnetic field ~ 26.0 T it can be associated with the interfacial region between the nanocrystallites or /and by presence disordered amorphous – like structure of some crystals [5].

The picks with maximums of HMF in the range of 40.0-51.5 T can reflect the presence of iron oxides and hydroxides in oxide films of investigated alloys. The intensities of these picks are small. It means that concentrations of iron in these compounds are small. Correct identification of these compounds at this step of investigations is difficult. More probable the simultaneous presence of iron compounds such as α–Fe_2O_3, Fe_3O_4, β–Fe_2O_3.and in the form of metallic iron and an unknown phase called as Fe^{4+}.

Figure 3. Quadrupole splitting distribution of Mössbauer spectra of ^{57}Fe in: a) oxide film of 2.2 μm on alloy (Zr-1.24 mas.%Fe) after 1136 h of corrosion, b) oxide film of 3.2 μm on alloy (Zr-1.39 mas.%Fe-0,60 mas.%Cu) after 8100 hours of corrosion.

Figure 4. Hyperfine magnetic distribution of Mössbauer spectra of ^{57}Fe in: a) oxide film of 2.2 μm on alloy (Zr-1.24 mas.%Fe) after 1136 h of corrosion, b) oxide film of 3.2 μm on alloy (Zr-1.9 mas.%Fe.0,60 mas.%Cu) after 8100 hours of corrosion.

Quadrupole splitting distributions (QSDs) are a further evolution in modeling Mossbauer spectra of oxides in which there are poorly-resolved quadrupole pairs. The QSDs model the local distortions and atomic disorder surrounding the Fe atoms in investigated samples. The differences in the shape of QSDs can be explained by presence of Cu atoms in Zr-Fe-Cu atoms. For binary alloy (Figure 3 a) three picks are visible with maximums ~ 0.2 mm/s, ~ 0.59 mm/s and ~ 0.8 mm/s. For ternary alloy (Figure 3 b) only two picks are visible with maximums ~ 0.1 mm/s, ~ 0.58 mm/s. For both oxide films the lines with QSDs in range 0.1-0,2 mm/s can be explained by presence of sold solutions of Fe^{3+} ions in ZrO_2. The QSDs with magnitudes ~ 0.58 mm/s and more can reflect the presence of sold solutions of Fe^{2+} ions in ZrO_2. The intensity of third pick in spectra of QSDs of oxide film of binary alloy is in the range of experimental error, but in all fitting it is visible. It is possible that some regions of ZrO_2 have iron ions in sold solution with great gradient of electrical field. This gradient deals with a distortion of structure of ZrO_2. The distortion of structure of ZrO_2 correlates with increasing of corrosion velocity of this alloy. The large width of QSDs for ternary alloy in the range of ~0.1 mm/s can result from probable existence solid solutions of iron ions Fe^{4+} in ZrO_2.

The relative content of iron in the form of so cold Fe^{4+} in the ternary alloy oxide films is greater than for binary alloy. These data allow us to make the assumption that the corrosion resistance is related to the content of iron in the form of metallic iron and probably an unknown phase called as Fe^{4+}. Thus the doping of the zirconium alloy by copper improves the corrosion resistance of the alloy and prevents the formation of large concentrations of compounds $\alpha-Fe_2O_3$.

4. Conclusions

1. Iron atoms in oxide film are investigated after corrosion test of binary Zr-Fe and ternary Zr-Fe-Cu alloys in autoclave at 350 °C of temperature and 16.8 MPa of pressure.

2. It is shown that the doping of copper in zirconium alloy with iron increases the alloy corrosion resistance and changes the process of iron atoms redistribution. In oxide films the compounds and

phase are detected such as 1) $\alpha-Fe_2O_3$, 2) $\alpha-Fe$, 2') solid solution Cu in $\alpha-Fe$, 3) solid solution Fe^{2+} in ZrO_2, 4) solid solution Fe^{3+} in ZrO_2, 5) unknown phase witch can be compound $ZrFe_2$.

3. It is revealed that in oxide films of ternary alloy having a higher corrosion resistance, the relative content of $\alpha-Fe$ is more in comparison with binary alloy. This result in conclusion that time of transition to catastrophic corrosion correlates with the formation of this phase in oxide films .The doping of copper in the alloy prevents the formation of iron oxides and increases the corrosion resistance of the ternary alloy.

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