Plasma-induced formation of hydrogen resistant oxide layers on zirconium surface

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Abstract. Features of plasma-induced formation of the surface oxide layers on zirconium alloy E110 (Zr–1%Nb) as well as hydrogen resistant properties of these layers are studied. It is shown that irradiation of the E110 sample with 1 keV ions of He + O₂ plasma produces the oxide layer depleted by oxygen nearby the surface. The onset of the intensive hydrogen penetration into the ion-irradiated sample during the steam test (673 K, 0.1 MPa) appears to occur 1500 hours later than into the untreated one.

1. Introduction
Fuel cladding tubes and other zirconium components of light-water reactor’s core absorb hydrogen due to interaction with water coolant and because of the impact of water radiolysis products (hydrogen atoms, ions, OH-radicals, etc.) [1]. Once the hydrogen solubility limit in zirconium is exceeded, the brittle hydrides begin to precipitate, leading to cracks propagation and severe material degradation [2, 3]. Hydride embrittlement of zirconium core components limits the lifetime and fuel burnup of existing reactors and prevents the power increase of future reactors. One of the perspective ways of hydrogenation protection of zirconium alloys is the surface modification by ion bombardment. It was revealed that structural changes made by ion flux in the surface oxide layer of zirconium alloy under some conditions provide the barrier properties of this layer, preventing hydrogen diffusion through it [4-6]. In this work, the features of the oxide layer formation on the surface of zirconium alloy E110 (Zr–1%Nb) under irradiation with 1 keV ions of helium plasma with oxygen admixture were investigated. Hydrogen resistant properties of the obtained layers were examined in water steam (673 K, 0.1 MPa) as well.

2. Experimental
The 7×7×1 mm³ tube sections of E110 zirconium alloy preliminarily rinsed in an ultrasonic ethanol bath were used as samples for the investigation. The surface oxide layers were produced on the samples by bombardment with ions of oxygen-containing helium plasma of the gas discharge with a hot cathode. The discharge with voltage 115 V and current 0.5 A was ignited at helium pressure of
0.7 Pa, oxygen pressure of $3 \times 10^{-2}$ Pa and residual gas pressure of $\approx 1 \times 10^{-3}$ Pa. The ions with the energy of 1 keV were delivered to the sample’s surface at a flux of $1.1 \times 10^{20}$ m$^{-2}$s$^{-1}$ during 10–60 min. Sample temperature upon the irradiation was $\approx 830$ K in all experiments.

The cross-section images of the irradiated samples were received using dual-beam scanning electron microscope FEI Scios equipped with the ion gun. To obtain a high-quality image a platinum layer was deposited on the surface. The surface oxide layers of zirconium were examined by X-ray photoelectron spectrometry (XPS) with profiling by ion etching in SPECS facility [7]. The energy and current of etching ions ($\text{Ar}^+$) were set at 3 keV and 10 $\mu$A, respectively. Zr 3d photoemission spectra were measured and decomposed into Gaussian-Lorentzian components. After that, the corresponding percentage of the identified components’ percentage in Zr 3d spectra on the etching time were considered as a qualitative equivalent of the depth profiles of these components.

Hydrogen trapping into the samples under ion irradiation was measured via thermal desorption spectrometry (TDS) in MIKMA facility [8]. TDS analysis consisted of the linear heating of a sample from $\approx 300$ K to 1500 K with the rate of 5 K/s and simultaneous measurement of desorption flux from this sample by the quadrupole mass-spectrometer. The amounts of hydrogen atoms in the samples were derived from the integrated TDS spectra (dependences of the desorption flux on sample temperature) of hydrogen-containing molecules ($\text{H}_2$, $\text{H}_2\text{O}$).

For comparison of the hydrogen resistant properties, both ion-irradiated and untreated samples were exposed to water steam at 673 K and 0.1 MPa for 40-3000 hours. The samples of both types were periodically withdrawn one-by-one from the steam ambient and underwent to TDS analysis. Some of the samples were analyzed by XPS.

3. Results and discussion

The experimental results have shown that the thickness of the oxide layer formed on zirconium surface under ion irradiation within the chosen range of irradiation times is limited to a couple of hundred nanometers due to sputtering. In particular, the oxide layer thickness after 20 min of irradiation was equal to $\approx 150$ nm (figure 1).

XPS profiling has revealed that the percentage of zirconium suboxide components (ZrO$_x$, $x<2$) in Zr 3d spectrum measured beneath the surface of the oxide layer of the ion-irradiated E110 sample exceeds that of the oxide layer formed on the sample in oxygen ambient without ion bombardment (figure 2).
This fact points at creation and accumulation of oxygen vacancies in the oxide layer under the irradiation. According to the TDS results, the trapping of hydrogen from residual gas into the E110 sample for 20 min of irradiation with 1 keV ions of He + O₂ plasma equals to ~3 × 10²³ m⁻³ that is less than 10% of the initial hydrogen content in the sample.

Figure 2. Percentage of the suboxide components, ZrOₓ (x<2), in XPS spectra of Zr 3d states vs etching time of the ion-irradiated E110 sample (□) and the one exposed to oxygen ambient (■).

Testing of the E110 samples in superheated water steam (673 K, 0.1 MPa) has indicated that the shape of time dependence of hydrogen absorption by the ion-irradiated sample (1 keV, 20 min) is similar to that of the untreated one (figure 3). One can see that in both cases, with increasing exposure time the hydrogen uptake remains negligible up to a certain point, but after that, the sharp acceleration of the zirconium hydrogenation is observed. The onset of the intensive hydrogen penetration into the untreated E110 sample came at 1000 hours of steam exposure whereas for the ion-irradiated one it occurred after 2500 hours.

Figure 3. Hydrogen concentration in the ion-irradiated E110 sample (□) and in the untreated one (■) vs time of their exposure to water steam (673 K, 0.1 MPa).

XPS profiling of both types of the samples, carried out after 500 hours of steam exposure, has revealed that the percentage of zirconium suboxide components in Zr 3d spectrum measured beneath the surface of oxide layer of the ion-irradiated E110 sample is still higher than that of the non-irradiated one (figure 4). Thus, the oxygen-depleted surface area of the oxide layer formed under ion bombardment persists after 500 hours of the steam exposure.

The apparent reason of mitigation of the hydrogen trapping into the samples irradiated with 1 keV ions of helium-oxygen plasma is the presence of anion vacancies in the surface oxide layer, which
appear under ion bombardment. Since the hydrogen transport through zirconium oxide carries out by hopping of hydrogen ion between the adjacent $O^2-$ ions [9], the increase of the anion vacancies’ concentration in the oxide lattice leads to decrease of the hydrogen hopping possibility. The stage of accelerated zirconium hydrogenation, however, comes at a certain point, and this fact may be a consequence of gradual disappearance of the oxygen-depleted surface area along with its barrier properties during the further oxidation.

![Graph](image)

Figure 4. Percentage of the suboxide components ZrO$_x$ ($x<2$) in XPS spectra of Zr 3d states vs etching time of the ion-irradiated E110 sample (□) and the untreated one (■) after 500 hours of their exposure to water steam (673 K, 0.1 MPa).

4. Conclusion
The irradiation of zirconium alloy E110 with 1 keV ions of helium-oxygen plasma results in formation of oxide layer, which is depleted by oxygen near the surface. During the subsequent exposure to superheated water steam, the onset of the intensive hydrogenation of the ion-irradiated sample occurs 1500 hours later than that for the untreated one. Mitigation of the zirconium hydrogenation is presumably caused by the presence of anion vacancies in the oxide layer which retard hydrogen transport through the oxide. Degradation of the barrier properties of the modified oxide layer may be a consequence of the gradual elimination of anion vacancies in it during the oxidation in steam. Apparently, the procedure consisting of sequential plasma-induced oxidation of zirconium alloy and deposition of a coating preventing oxygen penetration into the modified oxide layer may become a method of zirconium alloys protection against hydrogenation.

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