The impact of the initial state on the kinetics of oxidation ion-modified fuel cladding alloy E110

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Abstract. The paper examines the impact of the initial state (the presence of impurities, surface preparation), and surface alloying on the kinetics of the oxidation of fuel cladding alloy E110. The studies concluded that the use of ionic polishing instead of traditional chemical polishing helps to reduce the rate of oxidation of zirconium alloys. Also studied the effect of alloying elements introduced in the surface layers of claddings by ion mixing on the kinetics of the oxidation of the alloy E110.

1. Introduction
Increasing resistance to corrosion of fuel cladding alloys of zirconium in the working conditions of pressurized water reactors is an important task of modern reactor material science. A significant role in the kinetics of oxidation has surface quality (the presence of impurities, roughness) [1]. Currently used mechanical polishing of the outer surface of the fuel rods can not achieve high levels of surface roughness and wherein the surface is contaminated with abrasive particles. The use of chemical polishing significantly pollute surface residues of acids used for etching. In this regard, it proposed to use the method of ion polishing at the final stage of manufacture of fuel elements for cleaning the outer surface from dirt and upgrading of surface roughness.

2. Experimental methods
The samples cladding diameter of 9.15 mm and a wall thickness of 0.65 mm from several batches on the basis of E110 alloy (Zr-1%Nb). In comparison with the original alloy E110 in the part of the batches introduced impurity of nitrogen and carbon. Samples of each batch were divided into groups: the first group took only mechanical grinding, the second part of the samples was subjected to chemical etching and polishing in the electrolyte CH$_3$COOH + 10% NClO$_4$, and part of the samples was purified argon ion beam.

The doping of the surface layers of samples carried out by ion mixing of the deposited film by irradiation beams of Ar$^+$ ions with a broad energy spectrum on the "VOKAL" [2] (the average energy of the ions in the beam $<E>$ = 10 keV, the ion current density $j$ = 25 mA/cm$^2$, dose $F$= (1-5)$\times10^{18}$ ion·cm$^{-2}$, the temperature of the samples under irradiation $T$$\leq$200$^\circ$C, residual gas pressure $p$ = $1\times10^{-6}$ Pa).

After preparation and doping samples were tested in the autoclave with water at temperature of 350 $^\circ$C at a pressure of 17 MPa, which corresponds to the operating conditions of VVER reactors. At various stages of the autoclaving the samples were studied by scanning ion microscopy (SIM), which allows you to assess the condition and thickness of the oxide film.
3. Experimental results and discussions

It is known that oxidation processes are highly dependent on the surface topography. Developed relief significantly increases the area of interaction products with a corrosive environment, thereby increasing the rate of permeation of oxygen to the boundary of the "metal oxide". Measurement of surface roughness of the samples after preparation was conducted on the profilometer TR-200 (Japan). Value of roughness $R_a$ of the samples after mechanical grinding was $1.7 \pm 0.2 \mu m$ (Figure 1), after the chemical polishing $0.7 \pm 0.2 \mu m$. In samples subjected to argon ion polishing value of roughness ($R_a$) reached $0.6 \pm 0.1 \mu m$ (Figure 2).

![Figure 1](image1.png)  
**Figure 1.** Profilogram sample surface after mechanical polishing.

![Figure 2](image2.png)  
**Figure 2.** Profilogram sample surface after polishing ions $Ar^+$.  

Previous research of the state of oxide films have shown that the structure of the films in the main repeating structural features of the substrate, in consequence of which there is a different film growth rate in individual grains [3, 4]. Therefore, the presence of impurities and contaminants on the surface of the sample promotes violatehomogeneity of the oxide film, an increase of internal stresses in the oxide, and as a result, poor adhesion of the oxide to the metal substrate. The presence of contaminants on the surface of the samples was determined by X-ray fluorescence analysis, which showed the presence of significant amounts of chlorine and carbon on the surface of samples after the chemical polishing. For samples that have passed the ion cleaning and polishing the presence of impurities on the surface is minimal.

Autoclaved test of the samples were carried out during 4320 hours. To study the influence of the initial state on the oxidation kinetics, oxide films of the samples were researched after 300, 720 and 2160 hours of oxidation. SIM method used to measure the thickness of the oxide film, was determined presence of pores, cracks and inclusions on the surface and in the bulk oxide (Figures 3, 4).

![Figure 3](image3.png)  
**Figure 3.** Photograph of a cross structure of the oxide film of the sample after the mechanical grinding and autoclave test for 4320 hours.

![Figure 4](image4.png)  
**Figure 4.** Photograph of a cross structure of the oxide film of the sample after the chemical polishing treatment + $Ar^+$ ion beam and autoclave test for 4320 hours.
As shown in Table 1 for the first 720 hours of oxidation on all samples of E110 alloy grows homogeneous solid oxide film regardless of the method of surface preparation. However, the use of ion treatment external surface slows down its rate of growth. After 2160 hours of autoclave tests in samples of untreated and polishing of the ion beam in the oxide film are formed pores and cracks that occur due to internal stresses in the oxide caused by microscopic irregularities of surface topography and the presence of contaminants and undesirable impurities.

Table 1. Results of the autoclave test.

|                | mechanical-polishing | chemical-polishing | mechanical-polishing + ion polishing | chemical-polishing + ion polishing |
|----------------|----------------------|--------------------|-------------------------------------|-----------------------------------|
| 300 hours of autoclave test | Oxide thickness – 1.0±0.1 µm, No pores | Oxide thickness – 0.9±0.1 µm, No pores | Oxide thickness – 1.0±0.1 µm, No pores | Oxide thickness – 0.8±0.1 µm, No pores |
| 720 hours of autoclave test | Oxide thickness – 1.6±0.1 µm, No pores | Oxide thickness – 1.3±0.1 µm, No pores | Oxide thickness – 1.3±0.1 µm, No pores | Oxide thickness – 1.2±0.1 µm, No pores |
| 2160 hours of autoclave test | Oxide thickness – 2.1±0.1 µm, Pore density – 0.5% | Oxide thickness – 1.7±0.1 µm, Pore density – 0.5% | Oxide thickness – 1.7±0.1 µm, No pores | Oxide thickness – 1.7±0.1 µm, No pores |
| 4320 hours of autoclave test | Oxide thickness – 3.8±0.1 µm, Pore density – 2.0% | Oxide thickness – 3.0±0.1 µm, Pore density – 2.5% | Oxide thickness – 2.3±0.1 µm, Pore density – 0.5% | Oxide thickness – 1.9±0.1 µm, No pores |

The presence of pores and cracks in the bulk oxide facilitates the penetration atoms of oxygen to the boundary of the "metal oxide", which causes the acceleration of the kinetics of oxidation of the samples that passed the mechanical and chemical polishing of the surface, which significantly according to the thickness of oxide films of the samples after 4320 hours of autoclave tests. In addition, the presence of pores in the oxide causes an increase in internal stress, which leads to the further development and increase the number of voids in the oxide film. Samples of special melting E110 alloy with impurities of carbon and nitrogen, depending showed similar growth rate of the oxide film, depending on the initial state of the surface, but have a lower corrosion resistance as compared with the reference samples of E110 alloy.

4. Conclusion

The experiments confirmed the considerable influence of the surface state and the ways of its preparation on the kinetics of oxidation zirconium alloys. It is shown that mechanical grinding cannot produce sufficiently high surface roughness in comparison with the chemical polishing and surface treatment of ionic claddings. Also, because a sufficiently high ductility alloy E110 during mechanical polishing are abrasive particles. As a result, the corrosion resistance of E110 alloy is reduced due to the state of the surface.

Chemical polishing allows to achieve high values of surface roughness, however, for improving the corrosion resistance needs to cleaned the surface from impurities remaining from the etchant, such as chlorine and carbon.

Surface claddings argon ion beam, as a final step of manufacturing the fuel elements can slow the growth rate of the oxide film on the outer surface of the fuel cladding of VVER reactors by 30-40% due to the removal of impurities and smoothing the microscopic irregularities of the relief, the remaining after mechanical polishing. Thus, application of the technology of ion polishing in addition to mechanical polishing or chemical polishing can significantly improve corrosion resistance of the alloy product E110.
Acknowledgements
This work was performed within the framework of the Center of Nuclear Systems and Materials supported by MEPhI Academic Excellence Project (contract № 02.a03.21.0005, 27.08.2013).

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