Legitimacies of the growth of oxide films on ion-modified samples from the alloy E110 at high-temperature oxidation

B A Kalin, N V Volkov, R A Valikov, A S Yashin and D N Ignatiyev

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

E-mail: nvvolkov@mail.ru

Abstract. The possibility to obtain barrier layers during the surface modification by ion-plasma to decrease the oxidation and hydrogenation rate of fuel claddings from zirconium alloys at various operation conditions is studied in this paper. Fuel claddings from the alloy E110 obtained on the outer surface of fuel elements after ion polishing are determined on the basis of calculations and experiments performed: the average ion energy in a beam is 3-4 keV, the ion current is 0.4-0.7 mA cm−2, and the total irradiation dose is 5×1018 ion cm−2. Cleaning and polishing of samples from the alloy E110 were carried out on the installation ILUR-03 by a radial beam of argon ions with a wide energy spectrum. Thin films (up to 100 nm) of alloying elements – Fe, Al, Mo, Y, Mg, and Cr were obtained on the polished surface by magnetron deposition and then implanted into the near-surface layer under the influence of a radial beam of argon ions. Study of the element composition of cleaned and modified near-surface layers was performed by X-ray microanalysis. A part of the samples was preliminarily autoclaved in distilled water at the temperature of 350 °C and the pressure of 17 MPa for 500 h to obtain a protective layer from an oxide film enriched by implanted elements. It is shown that alloying elements are mostly located at the oxide-metal boundary and in the oxide.

1. Introduction
The surface modification of materials by ion beams is one of the most effective and precise methods of increasing the service properties of articles. For example, fuel claddings made from the zirconium alloy E110 with an ion-modified surface can exhibit a much higher corrosion resistance in reactor conditions (water medium, the temperature is 350 °C, and the pressure is 17 MPa) [1-3]. This is due to the formation of dense oxide films at the initial stages of oxidation. Ion polishing of the surface and alloying of the near-surface layer of the material by ion mixing can promote an increase of the protective properties of the oxide. The study of the oxide growth on an ion-modified surface in conditions of intensive high-temperature oxidation corresponding to the emergency regimes of the reactor (steam-water medium, the temperature is up to 1200 °C) is of particular interest. The integrity of the fuel cladding and the working capacity of the fuel element directly affect the safety of the reactor in these regimes.

2. Materials and tools
Fragments of fuel element tubes made from the alloy E110 (Zr-1% Nb) on the basis of sponge and having an optimized composition were used as samples for the research. The outer diameter of the samples was 9.15 mm, their wall thickness was 0.65 mm, and their length was up to 500 mm.
The outer surface of the samples was treated on the installation ILUR-03 by a radial beam of argon ions with an average energy of 3-4 keV. The ion current was equal to 0.4-0.7 mA cm\(^{-2}\) and the total irradiation dose was \(5\times10^{18}\) ion cm\(^{-2}\). The treatment of the samples included the removal of impurities of the sorbed material in the near-surface layer, polishing of the surface up to a roughness better than \(R_m=0.3\) \(\mu\)m, and alloying by ion mixing of the atoms of films preliminarily deposited on the surface of samples using magnetrons. Fe, Al, Mo, Y, Mg, and Cr of a purity better than 99.99 at.% were used as targets for magnetron sputtering. The film thickness did not exceed 150 nm. The scheme of the samples' treatment on the installation ILUR-03 is shown in Figure 1.

![Figure 1. Scheme of the treatment of tubes on the installation ILUR-03: a) cleaning and polishing by an ion beam, b) deposition of films of alloying elements by magnetrons, c) alloying of the near-surface layer by ion mixing.](image)

The prepared samples were exposed to corrosion tests in a water-steam environment at the temperature of 1200 °C for 100, 200, and 500 s. A part of the samples was preliminarily autoclaved in water at the temperature of 350 °C and the pressure of 17 MPa for 30 and 500 h. The oxidation degree of fuel claddings was estimated using a specific overweight \(\Delta m\) or a local depth of oxidation (LDO):

\[
\Delta m = 920 \times \exp\left(\frac{10410}{T}\right) \times \sqrt{t},
\]  

where \(\Delta m\) is the specific overweight of oxygen, mg cm\(^{-2}\); \(T\) is the temperature, K; and \(t\) is the time of oxidation, s. The LDO-parameter is determined experimentally or by calculation as the ratio of the total thickness of an equivalent zirconium layer, which would react with the steam, to the initial thickness of the fuel cladding:

\[
LDO = N \times \delta_e \times \delta_0 \times 100\%,
\]

where LDO is the local oxidation depth, \%; \(N\) is the coefficient that takes into consideration the two-sided oxidation of the fuel cladding, \(N=2\); \(\delta_e\) is the equivalent layer thickness (the calculated thickness of zirconium which would transfer to \(ZrO_2\)); \(\delta_0\) is the initial sample thickness. The samples were studied by optical and scanning ion microscopy, the element composition was studied by X-ray microanalysis.

3. Results and discussion

The appearance of the samples before and after the high-temperature oxidation is shown in Figure 2. The oxide film on all the samples has a smooth dark gray color with no visible signs of damage or crumbling.
Figure 2. Photos of the samples of fuel claddings with a diameter of 9.15 mm and a length of 10 mm made from the alloy E110: a) before and b) after the corrosion tests.

Figure 3 shows the dependence of the LDO-parameter on the oxidation time of samples with various states of the surface at the temperature of 1200 °C. As the analysis showed, the oxidation kinetics of the samples in the initial state complies to a parabolic law. The surface treatment of tubes by an ion beam results in a change in the character of dependencies. For this time range of the tube after the ion polishing and alloying by Al, lower LDO-values are observed. At that, a slowdown of the oxide growth on the alloyed sample is observed at the initial stage, which is probably due to the inhibition of the film growth owing to the redistribution of Al atoms in the oxide-metal system.

Figure 3. Dependence of the LDO-parameter of samples on the oxidation time at 1200 °C: 1) in the initial state; 2) after the ion polishing; 3) after the surface alloying by Al atoms. The dotted line shows the trend of the parabolic dependence of oxidation for the samples in the initial state.

The effect of the preliminary autoclaving of fuel tubes on the kinetics character of high-temperature oxidation of the material was studied. As can be seen from the data presented in Figure 4, the oxide film grown under autoclave conditions on the surface of samples in the initial state slows down the process of high-temperature corrosion, which is in agreement with the data of other researchers [4]. The samples with an ion-alloyed surface that were preliminarily oxidized show bigger values of the LDO-parameter in comparison with tubes that were not exposed to autoclaving, which can be seen in Figure 5. These results are presumably connected with the evolution of the modified layer of a material in the process of oxidation at 350 °C. At this stage, Al atoms are redistributed in the oxide-metal system and suppress the oxide film growth in the specified temperature range.
Figure 4. Dependence of the LDO-parameter of samples on the oxidation time at 1200 °C: 1) in the initial state; 2) after preliminary autoclaving at 350 °C for 500 h.

Figure 5. Dependence of the LDO-parameter of samples after ion alloying by Al atoms on the oxidation time at 1200 °C: 1) without preliminary autoclaving; 2) after oxidation at 350 °C for 30 h.

4. Conclusion
The behavior of fuel tubes from the alloy E110 on the basis of sponge has been studied in the process of high-temperature oxidation. It has been shown that the ion modification of the surface using the regimes of polishing and alloying of the material by ion mixing of preliminarily deposited films can suppress the growth rate of the oxide at temperatures up to 1200 °C.

References
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