INVESTIGATION AND MODIFICATION OF THE STRUCTURAL-PHASE STATE OF OXIDE FILMS ON ZIRCONIUM ALLOYS

N.V. Volkov¹, B.A. Kalin¹, V.A. Markelov², V.V. Osipov¹, Yu.V Pimenov³,

¹ National research nuclear university «MEPhI»,
² OAO VNIINM named after A.A. Bochvar, Moscow, Russia,
³ OAO «TVEL»

National research nuclear university «MEPhI», Kashirskoye shosse 31, Moscow 115409, Russia, +7(495)324-3165, E-mail: BAKalin@mephi.ru
**Introduction**

The resistance to corrosion, breaking, wear, fretting-corrosion and hydrogen embrittlement of fuel claddings is significantly determined by the structural-phase state (SPhS) of the surface layers of zirconium alloys. The structure of an oxide film, as an effective barrier to oxidation and hydrogenation, is defined by such a SPhS. The oxide film copies the surface topography of an alloy and shows its surface defects. For example, fig. 1 shows a typical structure of the oxide film topography (an image of the oxide surface is obtained by secondary ions) on a zirconium alloy: the surface is uneven (the oxide film on separate crystallites grows with various rates); pores and cracks are observed. It is possible to eliminate the disadvantages of the surface topography and change the SPhS of the surface layer by radiation-beam action (RBA) and ion modification [1-3].

![Fig.1. Typical structure of the oxide film topography on a zirconium alloy](image)

In this work, ion mixing under irradiation by a beam of Ar\(^+\) ions with a wide energy spectrum of a preliminarily applied multilayer (Al+Fe+Mo+Y) film on the substrate of zirconium alloys has been chosen as a method of RBA with the purpose to increase the operational properties of zirconium alloys E110 and E635. The use of Ar\(^+\) ion beams with a wide energy spectrum also makes it possible to perform purification and ion polishing of the surface (in this case the surface roughness \(R_a\) decreases from 1–2 to 0.2–0.4 \(\mu m\)) which are necessary before application of multilayer films.

The state of ion-alloyed layers of alloys [4] and oxide films on their surface after corrosion tests during up to 3000 h in a water-steam medium at the temperature of 350\(^\circ\)C and the pressure of 17 MPa has been investigated in this work. Regularities of penetration of oxygen and hydrogen atoms into ion-alloyed (modified) surface layers of alloys E110 and E635 during the oxidation have been also studied.
1. Experimental procedure

Alloying by ion-mixing was carried out on the installation VOKAL forming a beam of Ar+ ions with a wide energy spectrum in the energy range of 1–17 keV. The mean energy was 10 keV, the ion current changed in the 15–35 µA range and the sample temperature was 100–150 °C. The irradiation dose was equal to (1–2)×10^18 ion/cm² and depended on the depth of a preliminarily sputtered multilayer (Al-Fe-Mo-Y) film. Samples were oxidized in 12Cr18Ni10Ti steel ampoules at the temperature of 350 °C and the pressure of 17 MPa for 2, 10, 100, 300, 600, 1200, and 3000 h.

The oxide film thickness was determined by two methods: a gravimetric analysis based on the weight increment of samples calculated for the thickness of a sample using the ratio 1 mg/dm² = 67 nm; an optical method based on shift of interference peaks.

The alloying depth and the SPhS of modified layers of alloys and oxide films were carried out by the following methods and equipment: transmission electron microscopy (EMV-100, JEOL-250SX); X-ray structure investigations (DRON-3); scanning electron (HPI-600) and ion microscopy (Strata-235, Quantum-300); secondary ion mass-spectrometry (SIMS-660, Oxford-Link-330); Rutherford back scattering (EMY-5000); surface profilometry (PP-202, α-Step-50, TR-200) [1-4].

Based on investigations of corrosion resistance of materials carried out at “MEPhI”, the following elements Al, Fe, Mo and Y were chosen for ion alloying [5,6].

2. Experimental results

**Roughness and microhardness of a surface.** The structural-phase state of a surface layer changes and its microhardness increases during ion mixing alongside with implantation of alloying elements from a preliminarily applied film, and a definite surface relief is formed owing to sputtering (the value of roughness Ra). There is polishing of the surface under certain regimes. The microhardness of zirconium alloys grows by 20–30 %. This increase depends on irradiation conditions (the density of an ion current, the pressure of residual gases in the working chamber).

The effect of “ion polishing” of the alloy E110 is observed (table 1) at the current of an Ar+ ion beam of 30–50 µA/cm² and the pressure of residual gases lower than 1 Pa (in case of alloying by Al and Fe atoms). At that, the value of Ra decreases from 0.8 to 0.3–0.5 µm. As to the alloy E635, the effect of “ion polishing” is observed only under joint irradiation by ions of Ar⁺ and He⁺ in the range of irradiation dozes of 1×10^17–3×10^19 ion/cm².

<table>
<thead>
<tr>
<th>Implanted atom</th>
<th>Initial state</th>
<th>Ar⁺</th>
<th>Al</th>
<th>Fe</th>
<th>Nb</th>
<th>Mo</th>
<th>Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>E110</td>
<td>0.80±0.10</td>
<td>0.60±0.10</td>
<td>0.55±0.10</td>
<td>0.75±0.10</td>
<td>0.90±0.10</td>
<td>0.80±0.10</td>
<td>0.37±0.10</td>
</tr>
<tr>
<td>E635</td>
<td>0.75±0.10</td>
<td>0.70±0.10</td>
<td>0.75±0.10</td>
<td>0.80±0.10</td>
<td>0.90±0.10</td>
<td>0.90±0.10</td>
<td>0.60±0.10</td>
</tr>
</tbody>
</table>
The distribution of implanted atoms in depth is an important factor of formation of a specified SPhS. The content of implanted atoms of Al, Fe, Mo, and Y (the depth of analysis was 100±3 nm) was obtained by secondary ion mass-spectrometry (SIMS). At that, the relative change of the content of standard alloying components of alloys (Nb, Sn, etc) in the alloyed layer was estimated by comparison with references. A typical distribution of implanted atoms in the surface layer (for example, for the type 100 zirconium (Zr-100)) under simultaneous alloying by Mo-Y-Fe-Al atoms is shown in fig. 2. It is seen from the figure that as a result of ion mixing the penetration depth of alloying atoms into the zirconium substrate is up to 300–500 nm. It is necessary to note that penetration of Y atoms is less effective in comparison with atoms of Al, Fe, and Mo. The given data testify to effective penetration of the chosen alloying atoms in depths more than 100 nm under ion mixing. At that, a change of standard alloying components (Nb, Sn, etc) in the alloys Е110 and Е635 is within the limits of measurement errors.

![Fig. 2. Distribution of implanted atoms in the surface layer of a type 100 (Zr-100) zirconium sample under simultaneous alloying by Mo-Y-Fe-Al atoms](image)

Results of X-ray phase analysis have shown that if there are β-Nb precipitates in the initial state of the alloy Е110, then its alloying by atoms of Al, Fe, Mo and Y results in formation of precipitates of zirconium compounds such as Zr-Al, Zr-Fe, Zr-Mo and pure metals Nb, Al, Fe and Mo. For example, in the initial state of the alloy Е635, there are separate precipitates of 0.1–0.3 μm in size with density of \( N = (3-4) \times 10^8 \text{ cm}^{-2} \), both on the border and in the body of a grain.

Irradiation of samples by Ar\(^+\) ions and ion alloying result in dissolution of fine precipitates, which gives rise to decreasing the density of precipitates \( N = (2-3) \times 10^8 \text{ cm}^{-2} \) and their mean size slightly increases as a result of that.

An analogous behavior is observed for the alloy Е110. In the body of a grain of the alloy in its initial state, there are stitched precipitates (β-Nb) with a size less than 0.2 μm and a density of \( N = (1-2) \times 10^8 \text{ cm}^{-2} \). Irradiation and ion alloying result in increasing their mean sizes up to 0.3 μm and decreasing their density \( N = (2-5) \times 10^8 \text{ cm}^{-2} \).
Oxidation of ion-alloyed samples of alloys. During oxidation of samples of zirconium and its alloys in the above-mentioned time intervals, the part of samples was withdrawn from ampoules to determine the thickness of oxide films and subsequently study their structural-phase state.

In oxidation of samples in the initial state for 10 h, the mean thickness of an oxide film on zirconium Zr-100 was 110 nm, and on E110 and E635 alloys it was equal to 150–170 nm. Irradiation of zirconium by Ar\(^+\) ions and its alloying by one of the chosen alloying elements increase, as a rule, the thickness of oxide films, the minimum increase being observed for samples alloyed by Al atoms up to 130 nm. In case of simultaneous complex alloying of zirconium and its alloys, a change of the oxide film thickness has more complex character, and in number of cases a decrease of the oxide film thickness is observed, for example, in alloying of the alloys E110 by Al+Mo atoms (up to 110–150 nm) and E635 by Fe+Mo atoms (up to 140 nm).

In case of big time intervals of oxidation of samples in the initial state, an increase of the thickness of oxide films, as it is seen from fig. 3,a, changes according to the power law \( z = a_1t^n \), where \( n \leq 0.5 \), the maximum rate of the oxide growth being observed on samples of the alloy E635 and the minimum one on technically pure zirconium.

![Graph showing oxide film thickness growth](image)

Fig. 3. Changes of the oxide film thickness grown on the surface of zirconium and its alloys (data of overweights): a – in the initial state, b – after ion alloying by Al-Fe-Mo atoms (the power dependence curve is shown by a dotted line, \( \sim t^{0.33} \))

In oxidation of samples alloyed by ion mixing (hereinafter, ion-alloyed samples), the growth rate of films, as it is shown in fig.3.b, can be approximated by two linear curves. For the oxidation time interval of 10–600 h, the growth rates of an oxide on all the samples are approximately equal, and the oxide thickness from the oxidation time obeys the equation \( z(t) = A_1t + B_1 \). When the oxidation time is 1200–3000 h, the growth rate of an oxide (i.e. a change of the oxide thickness) decreases. At that, the oxide thickness on the alloy E635 is also bigger than that on the alloy E110.

As a whole, at big oxidation times (3000 h) the thickness of an oxide film for both the alloys has close values (1700–2000 nm). It allows making the assumption that in increasing the oxidation time of ion-alloyed surfaces the growth kinetics of an oxide film is determined by alloying conditions and, to a lesser degree, depends on the composition of an initial alloy, the minimum increase of the film thickness taking place on samples which were alloyed using the regime of simultaneous complex (Mo-Fe-Al-Y) alloying.
At the initial stage of oxidation (up to 100 h at thicknesses of a film up to 300 nm) the structure of films was studied by methods of optical, transmission and scanning microscopy. It was shown in [5, 6] that the structure of films mainly repeated the features of the substrate structure. A slight difference in the growth rate of films on separate grains is observed. In a thin oxide film growing in the area where the second phase particles of an alloy come out onto its surface, zones with an increased content of components forming these phase precipitates are formed. A detailed study of the zones structure testifies that they have complex (ring) structure and it is apparently determined by the compression stresses arising at growth of zirconium dioxide (ZrO₂). At that, the most density of the oxide zone is found on the external border of a ring close to which a developed dislocation grid formed as a result of relaxation of compression stresses is observed. The density and diameter of zones decrease during the ion alloying, for example by atoms of Mo or Al+Mo, and the concentration of these zones on the surface of samples increases with the atomic mass of alloying elements in the following sequence of Al→Fe→Mo.

An analysis of the results of electron-diffraction investigations of oxide films on ion-alloyed samples and samples in the initial state has shown that the oxide film with a small thickness is formed in the form of monoclinic crystal (pseudo-monocrystal) modification. An increase of interfacial distances and appearance of new intense lines typical for oxides of zirconium and implanted atoms, for example, Al₂O₃, Fe₂O₃, (Fe₃O₄), MoO, MoO₃, and Y₂O₃, are observed as a rule in films obtained on ion-alloyed samples.

The parameters of interplanar distances in an oxide film on samples simultaneously alloyed by Mo-Fe-Al are practically comparable with the parameters of an oxide on initial samples. At the same time, widening of point reflexes, which is apparently due to the presence of nanocrystallites Al₂O₃ and Y₂O₃ (15–30 nm) and the presence of residual internal mechanical stresses (compression in oxide, and tensile in metal), is found on electron-diffraction patterns.

*Scanning electron and ion microscopy of oxide films on a metal substrate.* Scanning (SEM) and optical microscopy was used to study the structure of oxide films at oxidation times of 300 and 600 h when the oxide film reached the thickness of 500–1000 nm. Typical results of SEM are shown in fig. 4. An analysis of the SEM-results has shown that a more uniform film is formed under complex simultaneous alloying of the surface of samples by Mo-Fe-Al-Y atoms (fig.4, c) in comparison with that obtained by alloying with Mo-Al-Y or Al-Fe atoms (fig. 4,b). At that, the surface roughness of the film decreases up to Ra ≤ 0.3 µm.

![Fig. 4. Photos of the oxide film surface after corrosion tests for 300 h (obtained by SEM): a – the type 100 zirconium, the value of the surface roughness Ra ≈ 0.8 µm; b – an E110 alloy sample alloyed by Al+Fe atoms, Ra ≈ 0.5 µm; c – an E110 alloy sample alloyed by Mo+Fe+Al+Y atoms, Ra ≤ 0.3 µm](image)
with a Ga-ion beam) was used to study the structure of oxide films, which made it possible to discover peculiarities of the film structure directly located on a metal substrate.

Oxide films grown on samples in the initial state have a columnar structure with a typical cross size of columnar crystallites of 200–300 nm, the oxidation front is not equal. Oxide films obtained on an ion-alloyed surface of alloys are significantly different, they have two main layers:

- The top layer up to 200–400 nm in thickness is pseudo-monocrystal, its thickness coincides with the extension of the area of radiation action under alloying;
- The main layer is a fine-crystalline polycrystal with monoclinic structure of ZrO₂, its grain size changes from 100 to 300 nm.

The main layer has a smooth boundary with a lower located so-called “oxide-metal” (the diffusion zone of oxygen) transition layer. A smooth decrease of the oxygen content from 1–2 at% to its “background” value is typical for the main layer.

As an example, cross sections of oxide films grown on the surface of a sample of the alloy E110 in the initial state (fig. 5,a) and simultaneously alloyed by Mo+Fe+Al+Y atoms (the “oxide-metal” boundary is shown by the arrow in fig.5,b) after corrosion tests for 600 h are shown in fig.5.

![Fig. 5. Structure of the oxide film obtained as a result of corrosion tests of the alloy E110 for 600 h (by SIM-Ga): a – the metal surface was in initial state (the horizontal arrow shows the vertical boundary of a columnar crystal), b – the surface is alloyed by Al+Fe+Mo+Y atoms (the vertical arrow shows the transition layer in the “oxide-metal” boundary)](image)

Redistribution of implanted atoms during oxidation of ion-alloyed samples. As an example, the distribution of implanted atoms of Mo, Fe, Y, and Al in the “oxide-metal” system after oxidation of samples of the alloys E110 and E635 in a water-steam medium for 300 and 600 h is shown in fig.6. It is seen from figs 6,a and 6,c that an increased content of implanted atoms (concentration of Al – 0.07±0.03 at%; Fe – 0.5±0.1 at%; Mo – 0.1±0.03 at%; Y < 0.05±0.03 at%) is observed at depths more than 500 nm. It is also necessary to point out that there is a presence of the second maximums of the concentration of Fe and Mo atoms at a depth X = 700–800 nm, Y atoms – X ≈ 300–350 nm. Appearance of the second maximum
C(X) for Y seems to be connected to a change of the ratio of oxygen concentration at the "metal-oxide" boundary, and for Fe and Mo it is due to diffusion processes and needs additional investigations.

Redistribution of implanted atoms is observed with increasing the time of corrosion tests, i.e. a typical dome-shaped form (figs 6,b and 6,d, the time of tests is 600 h) transforms to a more complicated dependence.

Distribution of oxygen atoms also has some heterogeneity which to a greater extent becomes apparent for the alloy E635 (the time of tests is 1200 h) and is located at a depth of 1200 nm, i.e. in the area of the first maximum in distribution of Fe atoms (the time of tests is 600 h).

Fig. 6. Distribution of implanted atoms in oxide films at various times of oxidation (measured by SIMS): a – 300 h, alloy E110 , b – 600 h, alloy E110, c – 300 h, alloy E635, d – 600 h, alloy E635
3. Discussion of experimental results

An analysis of data of changing the oxide film thickness, the distribution of implanted elements and oxygen atoms in a film from the oxidation time shows that the growth rate of an oxide film noticeably decreases at oxidation times bigger than 1200 h as a result of modifying the surface layer of zirconium alloys by alloying in comparison with the standard (initial) state of the alloys.

At the start of investigations (less than 1200 h), the corrosion of modified materials is characterized by a big overweight and a big thickness of the oxide film. When the oxidation time is bigger than 1200 h, a complex (simultaneous) alloying of materials by Al+Fe+Mo+Y using the ion mixing slows down the corrosion. The following model of the corrosion development has been proposed to describe such a behavior of the modified alloys.

Initial moments of the model are the following assumptions. At least two independent processes take place during simultaneous alloying and implantation of Al, Fe, Mo, and Y atoms into the materials. Firstly, ion bombardment and implantation of atoms into the substrate result in accumulation of damages, breakup of atomic bondings of the surface atoms, i.e. in increasing the level of free atom energy. Secondly, significant internal (side) stresses conditioned by dilatation of the lattice by implanted atoms are formed as a result of implantation in a thin surface layer. The distribution character of internal stresses under implantation can be described by the following function [7]:

\[ \sigma = \sigma_y = \sigma_{0y} = \frac{E}{1-\nu} \left[ -\varepsilon_0 + \frac{1}{t} \int \varepsilon_z dz + \frac{12z}{t^3} \int \varepsilon_0^z dz \right] \]  

(1)

where integration is performed by the thickness \( t \) of an implanted layer from 0 to \( t \); \( E \) – Young’s modulus, \( \nu \) – Poisson's ratio; \( \varepsilon_0 \) – volume deformation of an elementary volume which is determined by an equation characterizing a difference of two items, i.e. product of the formation energy of an implanted atom (\( H_M \)) on the concentration of atoms \( C_M \) and product of the formation energy of vacancies \( H_V \) on the vacancy concentration \( C_V \):

\[ \varepsilon_0 = \frac{1}{E} \left[ H_M C_M(z) - H_V C_V(z) \right] \]  

(2)

A wide zone of compressive stresses is located in the area of maximum concentrations of Al, Fe, Mo, and Y atoms.

At the starting stage of oxidation, using a classical scheme of oxidation of zirconium and its alloys, \( H_2O \) molecules are adsorbed by the surface of a sample and, trapping electrons, dissociate on oxygen ions and protons:

\[ \text{□}^{2+} + 2e + H_2O \rightarrow O^{2-} + 2H^+ , \]
\[ 2O^{2-} + Zr \rightarrow ZrO_2 + 2e + \text{□}^{2+} , \]  

(3)

where □ is an anion (oxygen) vacancy; \( e \), an electron. Then oxygen dissolves in a metal, and a \( ZrO_2 \) oxide film is formed on the surface of a sample when the concentration of oxygen in the surface layer attains \( \sim 30 \) at% (\( \sim 7 \) wt.%). Newly formed \( O^{2-} \) ions diffuse through the film and, attaining the metal, increase its thickness. The film grows into the metal on initial samples of zirconium in the form of columnar crystallites.
At the start of oxidation, a “loosened” activated surface on modified samples promotes more active interaction of corrosion oxygen with zirconium atoms and this decreases the free energy level of atoms in the Zr-O₂ system, and internal compressive stresses promote deformation “retraction” of O²⁻ ions into the metal. In this case the directed ion flow \( J \) can be estimated by the formula [3]:

\[
J = \frac{4\nu}{E} C_o D^I \frac{r w}{\rho k T} \frac{\partial \sigma}{\partial z},
\]

where \( \frac{\partial \sigma}{\partial z} \) is a gradient of internal stresses; \( 2r \), an interatomic distance in zirconium; \( D^I \), a diffusion coefficient of oxygen in zirconium; \( w \), a diffusion activation energy; \( C \), an oxygen concentration in the surface layer; \( \rho \), a constant.

The growth conditions of an oxide film are such that the corrosion front sufficiently uniformly moves deep into the material, forming, as it was shown earlier, a uniform quasi-monocrystalline or amorphous film. The driving force of the corrosion process is determined by an excess of the free atom energy \( (\Delta G = \Delta G_{chem} + \Delta G_{elastic}) \) of a metal with the availability of a significant contribution of the elastic component of free energy owing to distortions of the crystal lattice. A noticeable displacement of implanted Fe and Mo atoms from an oxide to the “oxide-metal” boundary takes place during the growth of an oxide film. Displacement of Al and especially Y atoms is weaker in comparison with Fe and Mo atoms owing to a high affinity of yttrium and aluminium to oxygen \( (\Delta G(Y_2O_3) = -996, \Delta G(Al_2O_3) = -865, \Delta G(MoO_3) = -812, \Delta G(Fe_2O_3) = -452 \text{ kJ/g-at.}_\text{Me}) \) comparable with the affinity of zirconium – \( \Delta G(ZrO_2) = -1145 \text{ kJ/g-at.}_\text{Me} \). The displaced atoms decelerate the advancement of oxygen and the oxidation front deep into the metal. Relaxation of internal stresses takes place simultaneously with a growth of the oxide film and, consequently, the driving force \(-\Delta G_{\text{elastic}}\) decreases in relation to a rapid growth of the oxide.

Accumulation of displaced implanted atoms (hereinafter admixtures) on the front of an oxide formation and relaxation of stresses result in changing the kinetics of a film growth, i.e. decelerating the frontal growth of an oxide phase. The mechanism of such a deceleration seems to be related to crystallization of a melt in conditions of concentration supercooling which results in formation of a cellular structure. In our case, the growth conditions of an oxide phase in conditions of accumulation of foreign atoms close to an interface exchange the frontal growth of an oxide for a local one which starts with formation of a morphological instability on a relatively smooth interface in the form of a ridge of the oxide phase into the metal. This ridge is a nucleus of an oxide grain (crystallite) on the front of which such a great number of foreign atoms are accumulated that advancement of the front is stopped, foreign atoms are a brake for oxygen diffusion. There is diffusion redistribution of an excess of foreign atoms which move to the side surfaces of a nucleus, gathering round the oxide phase. This results in formation of a fine grain. Nearby growing grains have analogous conditions. A way for movement of oxygen into metal is opened after diffusion redistribution of foreign atoms from the front to the sides. Accumulation of oxygen in local areas of a metal results in formation of an oxide phase, from which foreign atoms are displaced to the periphery of a grain and limit its growth. As a result of that, a fine-crystalline oxide is formed and oxidation of zirconium is retarded.

To describe the migration of implanted atoms under oxidation, a mass transfer model of foreign atoms at the expense of bulk and grain-boundary diffusion is used [6]. The diffusion coefficient of implanted atoms during the oxidation of ion-alloyed samples was calculated using the following equation \( D_{\text{impl}} = \frac{(L - X_m)^2}{t} \), where \( L \) is the maximum depth at which the presence of implanted atoms is registered (0.1 at%); \( X_m \), the depth of radiation-stimulated migration of implanted atoms under irradiation. Calculated diffusion coefficients
of implanted Al, Fe, Mo, and Y atoms and penetrating atoms of hydrogen and oxygen as a result of oxidation are shown in table 2. It follows from the table that the value $D_{\text{impl}}$ is $\left(2-6\right) \times 10^{-14}$ cm$^2$/s for implanted atoms, $\left(2-3\right) \times 10^{-14}$ cm$^2$/s for hydrogen atoms, and $(2-4) \times 10^{-15}$ cm$^2$/s for oxygen atoms.

It is known that the coefficient of grain-boundary diffusion of foreign atoms is in the range of $D \approx 1 \times 10^{-3} - 1$ cm$^2$/s, which is several orders higher than the bulk diffusion coefficient ($D_v \approx 1 \times 10^{-19} - 10^{-16}$ cm$^2$/s).

Thus, an analysis of the diffusion coefficients of implanted atoms, of oxygen and hydrogen at oxidation times of 100–3000 h makes it possible to conclude that the growth of an oxide film on an ion-alloyed surface is a multistage process accompanied by the diffusion of oxygen and alloying elements both in bulk and along the boundaries of grains ($D_{\text{grain-boundary}} > D_{\text{impl}} > D_v$). A barrier layer is formed in the oxide at oxidation times bigger than 600–1000 h. It consists of a fine crystalline ZrO$_2$-phase of monoclinic modification.

### Table 2

Calculated diffusion coefficients $D_{\text{impl}}(3000 \text{ h})$ cm$^2$/s of ion-implanted atoms and penetrating atoms of hydrogen and oxygen

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>Fe</th>
<th>Mo</th>
<th>Y</th>
<th>H-atoms</th>
<th>O-atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\left(2.5\pm1\right) \times 10^{-14}$</td>
<td>$\left(4.3\pm1\right) \times 10^{-14}$</td>
<td>$\left(1.7\pm1\right) \times 10^{-14}$</td>
<td>$\left(5.8\pm1\right) \times 10^{-14}$</td>
<td>$\left(2.5\pm1\right) \times 10^{-14}$</td>
<td>$\left(3.7\pm1\right) \times 10^{-15}$</td>
</tr>
</tbody>
</table>

### 3. Conclusion

1. It has been obtained that using the regime of ion mixing it is possible to implant alloying atoms of Al, Fe, and Mo from a multilayer film into zirconium alloys E110 and E635 to depths up to 0.3–0.5 µm and to concentrations exceeding the equilibrium solubility. At that, homogenization of the structural-phase state of a modified layer takes place; the roughness of a surface decreases and its microhardness increases by 20–30%.

2. A comparative analysis of the structure of oxide films growing on an ion-alloyed surface and on the surface of samples in the initial state has shown that multicomponent alloying of the samples surface by atoms of Al, Fe, Mo, and Y significantly improves the structure of oxide films and the oxidation front becomes even. In doing so, the adhesion of films to the surface of a metal increases, violation of the “entirety” of the films is suppressed.

3. It has been shown that the oxide film growing on an ion-alloyed surface has several typical layers:
   - the top layer 200–400 nm thick is an amorphous oxide layer;
   - the middle layer 500–700 nm thick has a uniform fine-crystalline structure;
   - the bottom layer borders with the “metal-oxide” boundary and has a sharp smooth boundary followed by a diffusion area with a smooth decrease of the oxygen content from 1–2 at% to its background value (< 0.1 at%).

4. It has been found that at big oxidation times the formation of an oxide film on the surface of modified zirconium alloys does not practically depend on their composition and is significantly determined by the conditions of alloying.
References